CO-CONTINUOUS CERAMIC MATERIALS USED AS THERMAL BARRIERS IN ELECTRON-BEAM PHYSICAL VAPOR DEPOSITION

YOGESH KUMAR

Research Scholar, Dept. of Physics,

Sri Satya Sai University of Technology & Medical Sciences, Sehore, Bhopal-Indore Road, Madhya Pradesh, India

Dr. Sanjay Rathore

Research Guide, Dept. of Physics,

Sri Satya Sai University of Technology & Medical Sciences, Sehore, Bhopal Indore Road, Madhya Pradesh, India.

ABSTRACT:

This paper is focused on the basic properties of ceramic composite materials used as thermal barrier coatings in the aerospace industry like SiC, ZrC, ZrB2 etc., and summarizes some principal properties for thermal barrier coatings. Although the aerospace industry is mainly based on metallic materials, a more attractive approach is represented by ceramic materials that are often more resistant to corrosion, oxidation and wear having at the same time suitable thermal properties. Electron beam physical vapor deposition (EB-PVD) is the technology that helps to obtain the composite materials that ultimately have optimal properties for the space environment, and ceramics that broadly meet the requirements for the space industry can be silicon carbide that has been developed as a standard material very quickly, possessing many advantages. One of the most promising ceramics for ultrahigh temperature applications could be zirconium carbide (ZrC) because of its remarkable properties and the competence to form unwilling oxide scales at high temperatures, but at the same time it is known that no material can have all the ideal properties. Another promising material in coating for components used for ultra-high temperature applications as thermal protection systems is zirconium diboride (ZrB2), due to its high melting point, high thermal conductivities, and relatively low density.

KEYWORDS: thermal protection systems; ultrahigh temperature applications; EB-PVD.

INTRODUCTION

One branch of engineering that deals with the maintenance, development and study of airplanes and spacecraft is aerospace engineering, where research into materials for the construction of aerospace components is in continuous development. Although metals are the most widely used materials in aircraft components, discoveries in materials science, particularly in composite science and technology, have allowed the development of new materials for aerospace engineering [1,2]. Lightweight design of aircraft frames and engines with materials of improved mechanical properties can improve fuel efficiency, increase payload, and flight range, which directly reduce the aircraft operating cost [3–5]. The aerospace industry is based on the use of composite materials for both primary and secondary constitutional components such as engine nacelles, rocket motor castings, aircraft wings, antenna dishes, landing gear doors, center wing boxes, tall cones, engine cowls and others [6,7]. At the present time, the use of composite materials in the aerospace industry inspire in a positive way the development and outline of modern and complex aero vehicles. In this sense, the properties like high specific strength and individual stiffness together with other unique properties makes this type of materials very attractive and suitable for this kind of applications. A class of composite materials is classified as an advanced composite which is defined by metal matrix composites, high-performance fiber-reinforced polymers, and those most used in high-performance aerospace vehicles, and their properties are the ceramic matrix composites. This class of composite materials provide supplementary functional advantages, the most highlighted being the temperature resistance [8,9]. Using composite materials in developing parts of aero vehicles implies more than just replacing the metals or other regular materials, it is about the introduction of advanced materials which have a role in a multitude of features starting from new designs in morphological structures, which were initially not possible with traditional materials [10]. One of the problems in the development of some aero vehicles consists in obtaining parts that must have specific properties for the field of use. The most attractive characteristic of advanced composite materials is based on the high ratio between strength, which is a basic feature when speaking about aerospace, and weight which is another goal in this industry, compared to the metals frequently used in aerospace. Moreover, the production techniques are a very important subject in this field. Manufacturing components by using composite materials favors the production of numerous distinct structures [11,12]. When it comes to temperatures that can be reached in this field, the aerospace industry has an ultrahigh temperature class that is generally placed from 1600 ◦C and can reach up to 2200 ◦C. These temperatures require the use of materials that can withstand very high temperatures and also have exclusive mechanical properties.

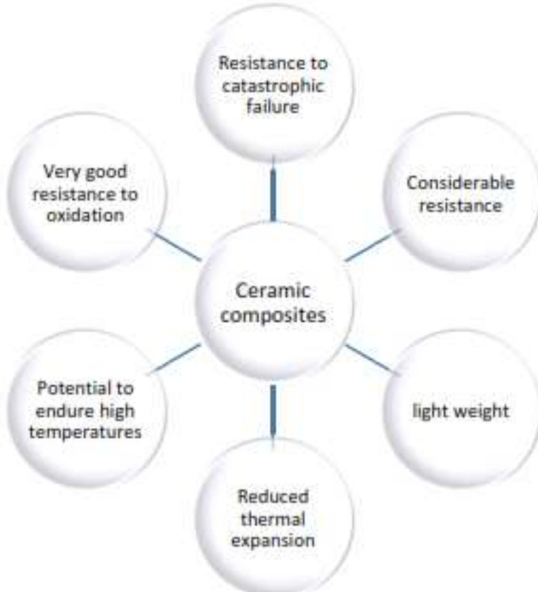

Figure 1. Properties of ceramic composites

Metallic composites are manufactured by reinforcing various types of metal matrices, such as titanium, aluminum, copper, magnesium, etc. Typical blends for metal composites are ceramic particle or fiber in particular, but carbon fiber or metallic fiber can also be used. When it comes to processing techniques, metal composites can be obtained by diverse methods such as casting and powder metallurgy, but with specific limitations because of the metallic use. This is despite the fact that there are limitations in the aerospace industry for metallic composites, the properties of which are presented in the Figure 2:

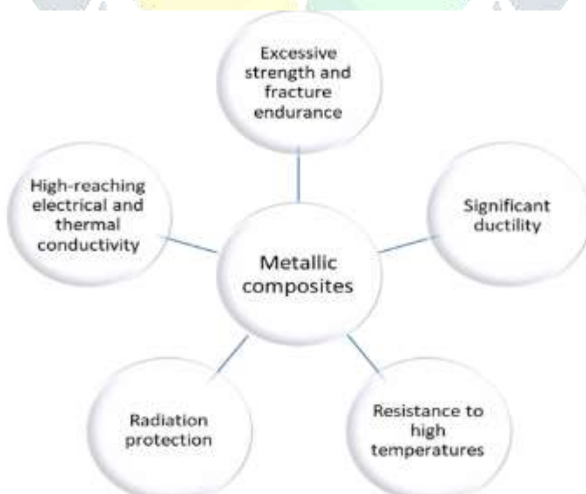

Figure 2. Properties of metallic composites

Another class of materials that have applications in the aerospace industry is represented by the ultra-high temperature ceramics. These materials are described as possessing a blend of properties that are characterized by very good and suitable mechanical properties and at the same time a significant meting point, which can reach up to 3000 ◦C and even exceed this value.

THERMAL BARRIER COATING

Thermal-barrier coatings are defined as ceramic materials that present suitable resistance at high temperatures. Components like metal turbine blades used in aircraft engines need to be covered by depositing thermal barrier which allow these engines to perform at high temperatures. The activity of these coatings is based on protecting from oxidation or melting because of that fact that hot gases from the engine core may affect the metal that is used at manufacturing these components for aero vehicles.

One essential role of thermal-barrier coatings components is to present various properties against the harsh environment such as corrosive atmosphere, high temperature and variation of this and complex stress conditions. It is well understood that it is complicated for a single coating component to possess all these conditions. At this level of depositing the coatings, the thermal barrier layers are planned to last for thousands of landings and take-offs in aero engines. When speaking about the complexity and diversity of thermal barrier coatings structures, there is an impediment of premature failure that can appear during operating conditions. At one point in time, the use of thermal barrier coatings decreased and moreover, their full characteristics were discredited. In order to avoid and eliminate these impediments, more detailed analyses were considered regarding materials, processing principles, performance and, not least, failure mechanisms were enhanced, in order to better understand how to respond beneficially. This research field presents associative subjects of materials science, chemistry, physics, mechanics and thermodynamics.

At the same time, the advantageous development of thermal barrier coatings is essential to bring improvements in the case of inlet gas temperature which leads to a boost of the performance of gas turbines. Hence, to develop thermal barrier coatings with interdependent features such as high resistance to sintering, low thermal conductivity and also phase stability, it is necessary to highlight the increased demands in order to obtain a proper final material. Commonly, thermal barrier coatings include a ceramic top coat and a metallic bond coat. The utilization of a bond coat is required to secure the metal substrate in the case of oxidation and corrosion because of the high temperature and also for coupling the ceramic top coat and the metallic substrate, being located between the substrate and the ceramic top coat. However, work has been published on the conventional thermal-barrier coatings system, which in fact contains three layers, covering the substrate. The first layer is the metallic bond coat, the second layer is the middle thermally grown oxide and the third layer is the ceramic top coat. Separately, these layers cannot provide the thermal and mechanical properties necessary for their use under special conditions, but which are directly proportional to the processing conditions that may impose modifications.

The first layer seems to possess critical characteristics, due to the fact that this layer performs two fundamental roles. The certainty of the coatings system starts with the first layer, in this sense, one role is to ensure a very good adhesion between the substrate and the ceramic top layer. The second function is to act in the case of severe oxidation, because the oxygen ions from the environmental conditions may pass through the ceramic layer, due to the porosity and high diffusivity. The top coat requires high thermal stability and low thermal conductivity. For these layers to act as demanded under special conditions at high temperatures, it is necessary that them to become common parts with the metal substrate that need coatings. For this reason, diverse physical methods were developed to deposit the ceramic top coat as a thermal barrier coating to the metallic substrate. The following methods are electron beam physical vapor deposition (EB–PVD), laser chemical vapor deposition, and atmospheric plasma sprayed, high-velocity oxy-fuel, sol-gel, plasma spray physical vapor deposition. One of the most used of these kinds of application is electron beam physical vapor deposition (EB-PVD) and the second is atmospheric plasma spray (APS).

ELECTRON BEAM PHYSICAL VAPOUR DEPOSITION (EB-PVD) TECHNOLOGY

The EB-PVD method is based mostly on the activity of the electron beam, which is considered the most important part having a role as thermal source in this deposition technique. One of the best and most attractive features of EB-PVD is the capability of depositing all types of material. The deposition procedure is based on the action of an electron beam established at 2000 ◦C within an electron gun, acting in accordance with the acceleration of thermal electrons supported by high voltage. The equipment includes a target of the material of interest, which is subsequently hit by high-speed electrons. Due to the energy generated by the electrons, the target material is melted and after that the material is transformed into vapor and deposited on the surface of the substrate as a coating. The highlighted advantage of this technique is the high deposition rate compared to other coating technique. The parameters applied for specific materials can be managed more easily and the surface also can be controlled when speaking about the dimension of the deposition. One mandatory property in obtaining the deposition materials is to present a strong adhesion between the coating and the substrate, which in the case of use of the EB-PVD technique, is fulfilled. Depending on the needs of the final material, the coatings can be deposited differently from ceramic to ceramic, metallic to metallic, ceramic to metallic, or metallic to ceramic.

Moreover, the best of the characteristic of this deposition technique is the multi material that can be used. In this sense, multilayer coatings can be deposited and also may be disposed of like alternative layers of distinct composition comprising ceramics, metals and polymers. All of these materials can be arranged as different and various layers on the substrate. Pointing to time efficiency, in this technique the deposition rate is high, and also in a short period the coating presents a dense structure. The microstructure may be controlled surrounded by a managed composition, trying to erase every possibility to be contaminated, and all of these properties are obtained finally regarding easily controlled parameters and flexible deposition. There are only minor exceptions where the deposited layers do not have a homogeneous microstructure, but generally the finished materials possess a good surface and uniform microstructure. Therefore, there is a fine relationship between the manipulating the process parameters and the final microstructure of the materials and also uniformity. Below are showed the schematic illustrations of electron beam physical vapor deposition (EB-PVD) equipment (Stage 1) and the generation of the film for coating (Figure 3).

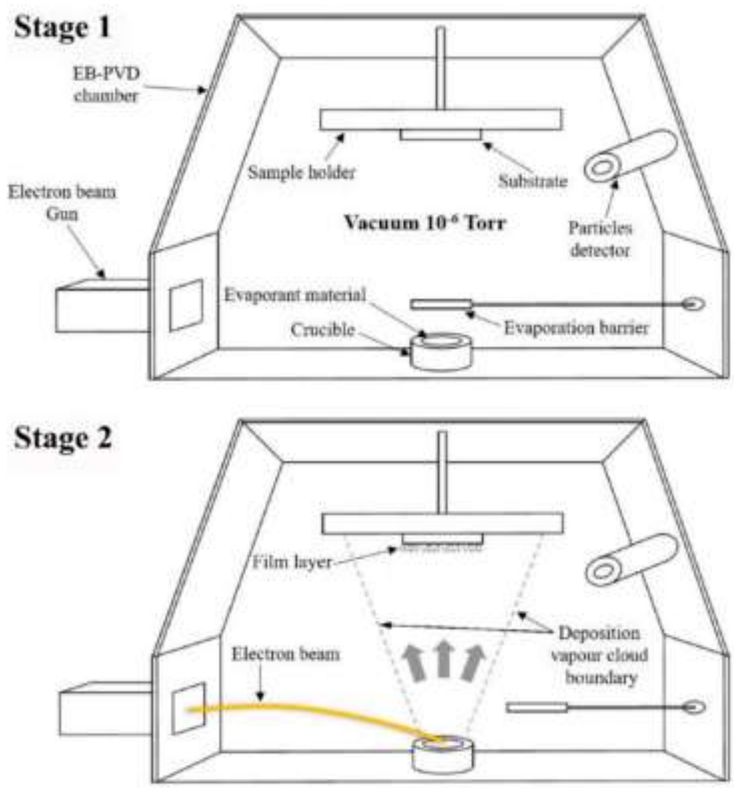

Figure 3. Schematic of electron beam physical vapor deposition (EB-PVD) equipment (Stage 1) and the generation of the film for coating

CERAMIC MATRIX COMPOSITES

Aerospace engineering includes an important part which is based on the choice of the materials for aero vehicles components. The requirements for a material vary simultaneously and in direct correlation with the specific component that possesses a suitable property for the aerospace industry. Some particular behaviors are being in consideration in materials selections when the design of a vehicle is desired. Each component is analyzed for design requirements which consist in manufacturability, loading conditions, maintainability and geometric limits. Aircraft engines are a point of interest in engineering this component. The most important aspects are the weight reduction and thrust improvement, which mandatory implicate materials with superior properties. The engine materials should present some specific features such as low densities which lead to weight reduction, and it is very important to possess essential mechanical properties under high-temperature conditions and an aggressive oxidative environment. Speaking about the design of an aircraft turbine engines, two divisions are described. The cold sections consist of the compressor, fan and casting, and the hot sections consisting of chamber, combustion and turbine. The category of cold and hot suggests that the sections present different temperatures, which affect the material selection where temperature is a crucial condition for aircraft engine materials. Corrosion resistant and high specific strength materials are suitable for use in the cold section.

Composites that include titanium or aluminum and polymers are optimal materials for the cold section. The temperature that is reached in this section is usually in the range of 500–600 ◦C. On the other hand, for the hot section the materials should present high temperature resistance, hot corrosion resistance and high specific strength. In this section, the temperature is usually between 1400–1500 ◦C. Titanium composite in this section cannot be used, in this case the suitable materials are nickel super alloys, due to their significant high temperature resistance strength.

The use of composite materials in aerospace vehicle engineering is about more than putting together the individual properties and increasing the final composite material characteristics and behavior. By means of using composite materials, the weight is reduced and the assembly is less complex. Moreover, the use of composite materials involves reducing fuel burn which is a major problem, and also reducing greenhouse gas emissions. Two methods can help to accomplish reduction in fuel burn. The first is about redicing the weight of gas turbine engines, and the second is about raising the thermal performance of the engines. As a matter of fact, composite materials are involved in both situations [2].

Carbon–Carbon Composites

Carbon–carbon composite materials are part of a category of materials that are called advanced composite materials, due to their properties. A large variety of shapes are characteristic to this type of materials starting from one-dimensional to n-dimensional (usually n = 1,2 or maximum 3), conditioned by the raw utilized material. By taking into account this benefit, the performance of the materials can be customized in direct contact with the applications. The first use of carbon–carbon composites was in the aerospace domain of applications; at the present time, this type of composites possesses various properties with applications in numerous sectors that brings them to the fore of research into ceramic composite materials.

For aerospace applications, carbon-based ceramic composites possess attractive properties, such as remarkable thermal stability and also low weight, making them the most favorable materials. Carbon fibers and the carbon matrix are basically components of engineered carbon–carbon composite materials, occasionally improved with different components. One attractive characteristic is the selection of the constituent materials and fiber orientations, which highlight the possibility to manage the properties of the final carbon–carbon composites. Generally, carbon–carbon materials and components are created at the same time, so that the final composite properties can be directed to increase the component capabilities. Resistance to oxidation at high temperatures, fracture toughness, strength and stiffness are principal characteristics of this composite carbon material.

Hafnium Carbide (HfC) Composites

Pointing to one of the most important properties in the aerospace applications, hafnium carbide (HfC) present the maximal melting point (~3950 ◦C) among the transition metal carbides. Another attractive feature is low vapour pressure, good ablation resistance and chemical inertness. Some recent publications reveal a new experience by introducing HfC compounds towards carbon–carbon composites. Wang et al. described the possibility of obtaining a hafnium carbide coating for carbon–carbon composite substrate by using the chemical vapor deposition method, and another coating for carbon–carbon composites by co-deposition of hafnium (tantalum) carbon using the same chemical vapor deposition technique. A different method was reported by Li et al. where the deposition of hafnium carbide on the carbon–carbon composites was possible by immersing the carbon materials in a hafnium oxychloride aqueous solution. To offer protection for carbon–carbon composites, hafnium and silicon carbide multilayers were deposited under low-pressure chemical vapour deposition as coatings.

Carbon/Silicon Carbide (C/SiC) Composites

Among the ceramic materials, silicon carbide (SiC) is placed as a first choice when a high-temperature environment is present. This material is used especially for structural components of aerospace vehicles such as transportation and nuclear areas, due to the fact that SiC possesses significant thermal conductivity, remarkable specific strength and superior tribology behavior at raised temperatures. Like any other material, it also has properties that do not meet the necessary conditions, such as low fracture resistance which limits in some cases the utilization of it in applications of interest. In this sense, given the subject discussed above, the carbon fiber-reinforced silicon carbine ceramic matrix composite materials seem to fulfill the requirements for high temperature applications. The fracture resistance is upgraded, and also the strength is increased with the supplement of high strength fibers.

Zirconium Carbide/Silicon Carbide (ZrC/SiC) Composites

Ultra-high temperature applications include the utilization of zirconium carbide (ZrC), as one of the best options due to the fact that the exceptional properties performed with suitable activity of the ZrC under harsh conditions. At high temperatures, the ZrC composite generate a refractory oxide scale which is another advantage when it comes to oxidation [14]. Transition metal carbides have considerable properties, being in the focus of the researchers for manufacturing aero vehicles components with required properties such as high melting point, high hardness and chemical stability, which are characteristics for zirconium carbide. Moreover, ZrC possesses features like impressive hardness which is mandatory for many cutting tools or/and abrasive industries. Numerous papers, place the zirconium carbide as a suitable material for elevated temperature applications due to high corrosion resistance.

Rocket engine nozzles and hypersonic vehicles components during their applications are in direct contact with aggressive environment. For this reason, the materials used in manufacturing these components have to present firstly a high melting temperature. Zirconium carbide ceramic is a promising material in this way. However, there are in this case some limits of the materials such as poor sinter ability because of the fact that ZrC possesses a reduced self-diffusion coefficient and strong covalent bonding. By a poor sinter ability is understood the fact that it is more complicated to reach a completely dense composites without a support from sintering additives. Because of the fact that ZrC ceramic composites may have limits in terms of their full activity under special conditions having poor thermal shock resistance and low fracture toughness, by adding SiC into ZrC the properties may be improved. The mechanical properties and oxidation resistance of ZrC are clearly enhanced after the incorporation of SiC, leading to the generation of a melted SiO2 layer at high temperature and also to the discrepancy of thermal expansion coefficient among ZrC and SiC.

CONCLUSION

Thermal-barrier coatings obtained by using the electron beam physical vapour deposition technique represent a way to improve the behavior of aero vehicles in high-temperature applications. The coatings have a significant role in assuring a barrier which acts in high-temperature environments. The performance of the thermal barrier is enhanced thanks to various ceramic coats deposited on the substrate. In order to choose suitable materials for aerospace applications, it has been proven that ceramic materials have properties that are mandatory for such applications. Ceramic materials possess low thermal conductivities and, for this reason, it is desirable for the manufacturing of components for aero vehicles to contain a large proportion of ceramic composites. The performance of the engine is increased, the temperature of the metal substrate is reduced and managed, and the lifetimes of the engines, hot sections and turbines are prolonged only by covering with thermal-barrier coatings. The selection of materials for acting as a thermal barrier is based on the evaluation of the materials. Basic requirements are mandatory such as high melting point, low thermal conductivity, and chemical inertness, good adherence to the metallic substrate, high-temperature resistance, high strength and resistance to oxidation at high temperatures. However, until now, no single material can achieve all of these mandatory conditions.

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