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An overview on novel thermal barrier coatings*

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Abstract: Thermal barrier coatings (TBCs) offer the potential to significantly improve efficiencies of aero engines as well as stationary gas turbines for power generation. On internally cooled turbine parts, temperature gradients of the order of 100－150℃ can be achieved. TBCs, typically consisting of an yttrium stabilized zirconia top coat and a metallic bond coat deposited onto a superalloy substrate, are mainly used to extend lifetime. Further efficiency improvements require TBCs being an integral part of the component which requires reliable and predictable TBC performance. TBCs produced by electron beam physical vapor deposition (EB-PVD) or plasma spray (PS) deposition are favored for high performance applications. The paper highlights critical R&D needs for advanced TBC systems with a special focus on reduced thermal conductivity and life prediction needs. To further enhance the efficiency of gas turbines, higher temperature and a longer lifetime of the coating are needed for the next generation of TBCs. This paper presents the development of new materials, new deposition technologies, and new concept for application as novel TBCs. This paper summarizes the basic properties of conventional thermal barrier coatings. Based on our own investigation, we reviewed the progress on materials and technologies of novel thermal barrier coatings. Except yttria stabilized zirconia, other materials such as lanthanum zirconate and rare earth oxides are also promising materials for thermal barrier coatings. Nanostructure thermal barrier coating is presented as a new concept. This paper also summarizes the technologies for depositing the thermal barrier coatings.

Key words: thermal barrier coatings; nanostructure; ceramic materials; deposition methods

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1 Introduction

In today's engines, the hot gas temperatures exceed the melting point of the Ni-base alloys substrate by more than 250℃. Actual metal surface temperatures are about 1000℃ with short-term peaks as high as 1100℃. Obviously the melting point of the alloys clearly marks the limit for future developments. Nevertheless, further increases in thrust-to-weight ratio of next generation aero engines will require even higher gas temperatures. Currently, engine design still primarily relies on lifetime extension benefits of TBCs. It is, however, obvious that prime reliant TBCs with predictable life-time performance are required to imple-

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ment TBCs as designed-in components and in this way to fully exploit their potential for significant performance improvements[1,2]. This paper highlights the present status and sheds some light on future developments in the area of thermal barrier coatings (TBCs). During the past decade, research efforts were devoted to the development and manufacturing of ceramic thermal barrier coatings (TBCs) on turbine parts because the traditional turbine materials have reached the limits of their temperature capabilities. The working parts of aircraft jet engines are subjected to serve mechanical, chemical and thermal stresses. Several thermal barrier coatings such as $CaO/MgO+ZrO_2$, YSZ, CeO_2+YSZ, and $La_2Zr_2O_7$, etc. have been evaluated as TBC materials. The selection of TBC materials is restricted by some basic requirements: (1) high melting point, (2) no phase transformation between room temperature and operation temperature, (3) low thermal conductivity, (4) thermal expansion match with the metallic substrate, (5) good adherence to the metallic substrate. So far, only a few materials have been found to basically satisfy these requirements[3,4]. This paper reviews the ceramic TBC materials and is helpful to the selection of TBC materials. The development of novel nanostructure TBCs concept is presented. The following are TBC materials and deposition methods under investigation. Among TBC's properties, thermal expansion coefficient and thermal conductivity are the most important. These data are collected from different references and our own investigation result. The advantages and disadvantages of other TBC materials are compared with YSZ on below. The deposition techniques of YSZ coatings are also summarized on below[5,6].

In this paper, we present an overview of various interesting materials, new concept, and new deposition technologies for novel TBC systems. For most of the developments presented here, we have undertaken our own investigations. For some rare earth oxides materials, the development of plasma spraying process is our researching now. Nanostructure plasma spraying TBCs as a new concept is also our favorite.

2 Probe for TBCs

2.1 Conventional thermal barrier coating systems

TBCs usually consist of a duplex system as schematically shown in Fig. 1. The actual thermal barrier is a ceramic top coating with the prime function to reduce the heat transfer to the metallic substrate. For many years, yttria partially stabilised zirconia (YPSZ) has been the prime choice, because it reveals a low thermal conductivity. Furthermore, it also shows a relatively high coefficient of thermal expansion, which comes close to that of the metal substrate. In-between the TBC and the substrate, a metallic corrosion resistant coating is applied, which protects the substrate from oxidation and/or high temperature corrosion and provides the necessary adhesion of the ceramic to the airfoil material. These bond coatings are MCrAlY. During processing and in service, a thermally grown oxide (TGO) layer forms as a result of bond coat oxidation which often plays the most important role for the adherence of the TBC[7-9].

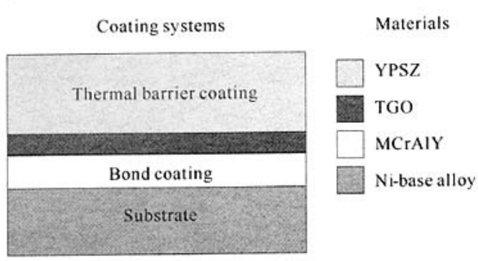

Fig. 1 Typical thermal barrier coating systems

2.2 Nanostructure thermal barrier coating systems

Nanostructured materials have demonstrated enhanced properties including hardness, strength, ductility and toughness. Due to these characteristics, nanostructured materials as a new concept may have an application as advanced thermal barrier coatings (TBCs). One of the biggest challenges in thermal spraying nanomaterials is to retain the preexisting nanostructure of the feedstock. During the plasma spraying of ceramics, it is necessary to partially melt the powder particles in order to achieve the necessary physical conditions for cohesion and adhesion. If nanostructured powder particles are fully melted during spraying, then the traditional behavior of thermal spray particles such as, solidification, nucleation and growth will take place[10,11]. Such processes will be able to destroy the original nanostructured features of the feedstock. Based on our own invetigation, the SEM photographs of the nanosturcture YPSZ feedstocks and YPSZ thermal barrier coatings via APS are given in Fig.2.

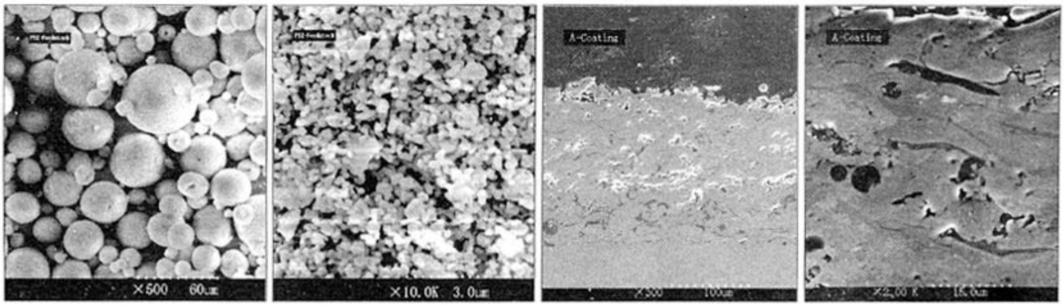

Fig.2 SEM photographs of the nanosturcture thermal barrier coatings via APS

3 Materials for TBCs

New materials for TBC means new chemical composition, which crystallizes in other structure types, compared to standard or modified zirconia[12-15].

3.1 Conventional YSZ

YSZ is the most widely studied and used TBC material because it provides the best performance in high-temperature applications such as diesel engines and gas turbines, and reports about this material are numerous. YSZ coating has been proved to be more resistant against the corrosion of Na_2SO_4 and V_2O_5 than that of the ZrO_2 coating stabilized by CaO or MgO. A major disadvantage of YSZ is the limited operation temperature ($<1473K$) for long-term application. At higher temperatures, phase transformations from the tetragonal (t) or non-transformable tetragonal (t′) to tetragonal and cubic (t+c) and then to monoclinic (m) occur, giving rise to the formation of cracks in the coating. On the other hand, these coatings possess a high concentration of oxygen ion vacancies, which at high temperature assist oxygen transport and the oxidation of the bond coat at the ceramic-bond coat interface, namely the formation of thermally grown oxide (TGO). This leads to spallation of the ceramic and such a mode of failure of the TBC is predominant when the coatings are thin as in gas turbines.

3.2 CeO_2+YSZ

CeO_2 has higher thermal expansion coefficient and lower thermal conductivity than YSZ, and the addition of CeO_2 into YSZ coating is supposed to be effective for the improvement of thermal cycling life. Remarkable improvement of thermal shock tolerability was attained by the addition of CeO_2 into YSZ. However, the addition of CeO_2 has some negative effects, such as the decrease of hardness and stoichiometry change of the coating due to the vaporization of CeO_2, reduction of CeO_2 into Ce_2O_3 and accelerated sintering rate of the coating.

3.3 $SrZrO_3$ and $BaZrO_3$

So far, only two materials with perovskite structure have been studied, i.e. $SrZrO_3$ and $BaZrO_3$. They have very high melting points (3073 and 2963 K, respectively), with thermal expansion coefficients being comparatively lower than that of YSZ. A former work about the TBC of $BaZrO_3$ proved that this coating did not show better thermal-shock resistance than YSZ. $SrZrO_3$ shows a phase instability which is expected to be detrimental to its thermal shock resistance.

3.4 $La_2Zr_2O_7$ and $Nd_2Zr_2O_7$

$La_2Zr_2O_7$ (LZ) was recently proposed as a promising TBC material. We have done an investigation on this crystal structure. The crystal structure consists of the corner-shared ZrO_6 octahedra forming the back bone of the network and La^{3+} ions. The holes which are formed by ZrO_6 octahedra can largely tolerate vacancies at the La^{3+}, Zr^{4+} and O_2-sites without phase transformation. Both La^{3+} and Zr^{4+}-sites can be substituted by a lot of other elements with similar ionic radii in case the electrical neutrality is satisfied, giving rise to the possibility of its thermal properties to be tailored. It is one of the few oxides with pyrochlore structure (such as $La_2Zr_2O_7$ and $Nd_2Zr_2O_7$) that are phase-stable up to their melting points. On the other hand, $La_2Zr_2O_7$ has even lower thermal conductivity than YSZ. However, the coating of this material did not give a longer thermal cycling life than YSZ coating which might be explained by its relatively low thermal expansion coefficient and poor toughness.

These two compounds have a melting point above 2000℃, they are stable up to the melting point and their thermal conductivities are significantly lower than the one of YSZ. Nevertheless the CTE is notably smaller than YSZ ($8.8-10.6\times K^{-1}$). $La_2Zr_2O_7$ and $Nd_2Zr_2O_7$ materials will become the most important novel thermal barrier coatings materials, and we will try our best to research these materials.

4 Technologies of TBCs deposition

There are essentially two processes which have emerged as viable ways to fabricate TBCs under industrial conditions. Plasma-spraying (PS) has been widely applied since the 1960s to produce TBCs on hot components like burner cans or combustion chambers. Plasma sprayed thermal barrier coating systems consist in most cases of a MCrAlY (M = Ni, Co) bond coat applied by vacuum plasma-spraying technique (VPS) and an atmospherically plasma-sprayed (APS) 7%-8% (mass fraction) YSZ top-coat. The performance of these systems mainly depends on the microstructure and hence the processing conditions of the coatings. The evaporation technology by means of electron beam physical vapour deposition (EBPVD) technology has emerged in the 1980s. The specific microstructure reveals a certain pseudoplasticity which translates into superior tolerance against straining and thermoshock, thus giving it a major edge inlifetime. Therefore, today EB-PVD is the process of choice as far as TBCs for high pressure turbine blades for aero engines are concerned, and becomes increasingly important also for turbine blades of land-based industrial gas turbines for power generation. During EB-PVD processing a high energy electron beam melts and evaporates a ceramic source ingot in a vacuum chamber. During evaporation the ingots are bottom-fed into the crucibles to ensure continuous growth of the ceramic coating[16]. Preheated substrates are positioned in the vapour cloud, and the vapour is deposited onto the substrates at deposition rates of 4-10 μm/min. To achieve defined stoichiometry of the zirconia a controlled amount of oxygen is bled into the deposition chamber. Recently, some process improvements have been introduced such as electron-beam preheating for large industrial components or in-line trolley installation for higher flexibility and throughput or dual-source jumping beam evaporation for generation of new types of TBC. In recent years, a number of alternative coating processes have been investigated, based on chemical vapour deposition (CVD), a technique with which columnar YPSZ coatings can be produced with a good throwing power and high deposition rates if metalorganic precursors or a plasma assistance are employed. Such processes could provide an easy way to evaluate new and/or complex ceramic compositions[17,18].

5 Future research and trends

Although TBCs are flying in today's advanced aeroengines and are introduced into first land-based gas turbines, a lot of research issues still have to be addressed until TBCs qualify to become prime reliant. Furthermore, advanced TBC systems have to be developed in order to accommodate the further anticipated increase in engine performance. In a recent critical R&D needs of TBCs in future gas turbine systems have been described as follows: reduced thermal conductivity; improved hot corrosion resistance; long-term thermal cycle testing in a thermal gradient; lifetime prediction modeling; non-destructive inspection technique development; process modeling/validation; modeling of long-term TBC system stability.

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