Thermophysical properties of selected powders for thermal barrier coatings

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ABSTRACT

Purpose: Plasma-sprayed thermal barrier coatings often have the problems of spallation and cracking in service owing to their poor bond strength and high residual stresses. Functionally graded thermal barrier coatings with a gradual compositional variation from heat resistant ceramics to fracture-resistant metals are proposed to mitigate these problems.

Design/methodology/approach: The results of measurements of thermal diffusivity by using one of the most modern experimental sets LFA 427 (Laser Flash Apparatus) produced by Netzsch Company. In order to measure the specific heat cp(T) and density p(T), two methods of thermogravimetry analysis were used STA 449 Jupiter F3 Netzsch Company and gas displacement density analyzer AccuPyc II 1340 Micromeritics Company.

Research limitations/implications: This paper presents the results of measurements of thermal diffusivity coefficient as a function of temperature for Sulzer powders, AMDRY 997, AMDRY 365C, METCO 45C NS, METCO 202 NS, METCO 204 NS.

Practical implications: Optimal technical and technological parameters of powders for thermal barrier coatings have been selected.

Originality/value: The presented method undoubtedly develops new possibilities for thermal barrier coatings.

Keywords: Thermal barrier coatings; Ceramics; Powder; Laser flash apparatus; Density; Thermal diffusivity

Reference to this paper should be given in the following way:

1. Introduction

Dynamic development of air civil transport requires the development of aircraft engines. It is directed to lower fuel consumption and reduction of pollution. To achieve those goals, it is necessary to employ higher exhaust gas temperature, which determines application of new materials characterized by higher heat resistance. The elevation of aircraft engines service temperature is possible through the use of turbine blades made of nickel superalloy with equiaxed microstructure (EQ), directional particle position (DS - directionally solidified) or with single-crystal microstructure (SC - single crystal). For surface protection of turbine blades high temperature resistant coatings could be deposited. They have a function of corrosion protection and thermal insulation of surface. Actually the thermal barrier coatings are used for this purpose. Thermal barrier coatings are used for protection of element's surface of hot section of an
aerospace engine. Those coating consist of, at least, two layers. Zirconium oxide stabilized by yttrium oxide is the outer layer. The inner metallic layer can consist of platinum-modified NiAl phase or multicomponent MeCrAlY alloy. The outer ceramic layer is applied using the plasma spray method under atmospheric pressure (APS) or physical vapour deposition involving ingot evaporation by electron beam (EB-PVD).

Thermal spraying is realized most often by application of high velocity oxy fuel or plasma spraying method. Air plasma spraying is used most frequently in industrial practice. The most commonly used material for ceramic layer of thermal barrier coatings is yttria stabilized zirconia [1]. From many years the new potential ceramic materials to replace YSZ were developed. The recent works describes few types of ceramic materials as: Al₂O₃, TiO₂, mullite, CaO/MgO+ZrO₂, YSZ, CeO₂+YSZ, zirconium La₂Zr₂O₇, etc. were assessed as TBC materials [2-5]. The most promising materials are perychlores, rare earth oxides and pervostkites. To develop new materials the analysis of physical properties is necessary. The most important factor is thermal expansion coefficient and thermal conductivity. The laser flash method enables to analyze properties of ceramic coatings and powders used for TBC’s application [6].

2. Experimental

Thermal conductivity and thermal diffusivity are the most important thermophysical material parameters for characterizing the thermal transport properties of a material or component. The Laser Flash technique is currently the most widely accepted method for precise measurement of the thermal diffusivity and the LFA 427 is the number one instrument on the world market (Figs. 1, 2). High precision and reproducibility, short measurement times, variable sample holders (Fig. 3) and defined atmospheres are outstanding features of LFA measurements over the entire application range from 20°C to 2000°C. The LFA 427 is the most powerful and versatile LFA system for research and development as well as all applications involving characterization of standard and high-performance materials in automobile manufacturing, aeronautics, astronautics and energy technology [7].
The applied impulse technique lets on the measurement of thermal conductivity and in range 0.001-10 m²/s, in the locker of the temperature 20-2000°C. Method of the correction of thermal losses also allow to the qualification for such materials at present how; materials in liquid state, composite about large dispersal, thin layers, many-layered materials, and also conductivity among layers (e.g. metal/form). The measurement of thermal conductivity is possible with exactitude 3%, and delimitation of thermal conductivity with supplied documentary evidence exactitude 5% in the whole measuring range. The device consists of several basic modules [7]. The working part allows to the safe work in laser radiation conditions and consists high- temperature furnace enabling the work in the temperature min. 1500°C and about the construction enabling maintenance of the high vacuum (pressure below 5·10⁻⁵ mbar), the carrier of samples with S-type thermocouple, the high power neodymium laser Nd: YAG and wavelength 1064 nm, cooled LN2, crystal set InSb and gear realizing the functions of the technical preparation of the measurement, production and maintenance vacuum, The control - measuring unit the of the demanded atmosphere gas circulation, cooling of the furnace folds etc. oneself from the arrangement of the acquisition of the data, the arrangement of the control of the temperature and powers of heating, arrangements protecting, transformer and the casing of the system. Software makes possible the device control by setting of measuring parameters, the control of the course of the measurement, the acquisition and data processing. It makes possible processing, analysis and the export data in the digital and graphic form. Analysis software contains standard mathematical models serving to the studies of measuring signals and the models of radiational losses leanings on the non-linear regress and the improved Cape - Lehman’s model. The device software contains the three layers materials model and the additional module of delimitation specific heat the comparative method realized in the device. Method of measurement of thermal conductivity by Netzsh LFA 427 consists in heating the sample of in the shape of the disc the short laser impulse to the flat surface, the growth temperature opposite of the sample’s surface sample follows in the result of what, measured in the function of time using the crystal set of infrared radiation (IR). Measured signal after the time partial growth of the temperature t₀,5 allow delimitation of thermal conductivity.

The coefficients thermal conductivity λ(T) counted on the basis of the example:

\[ \lambda(T) = a(T) \ \sigma p(T) \ \rho(T) \]  

(1)

The measuring exactitude which usually has to consider the mistakes of the qualification of remaining sizes thermophysical is not worse than the so-called exactitude of the „direct” methods of marking λ, consisting in the calculation of this size on the basis of the measurement of the thermal stream (through the gradients of temperature) and the geometrical parameters of sample near the foundation of the conditions of the stationary state.

Density of samples was measured by Micromeritic AccuPyc 1340 II Pycnometer (Fig. 4). The AccuPyc works by measuring the amount of displaced gas. The pressures observed upon filling the sample chamber and then discharging it into a second empty chamber allow computation of the sample solid phase volume. Gas molecules rapidly fill the tiniest pores of the sample; only the truly solid phase of the sample displaces the gas. A sample chamber of 1 cm³, 10 cm³, 100 cm³, can be selected to provide the best fit with your samples. The run precision mode allows you to achieve high repeatability. The instrument automatically purges water and volatiles from the sample and then repeats the analysis until successive measurements converge upon a consistent result.
In order to measure the specific heat \( c_p(T) \) were used thermogravimetric analysis STA 449 Jupiter F3 (Netzsch Company) (Fig. 5). The NETZSCH simultaneous thermal analyzers can be used to measure the mass change and transformation energetics of a wide range of materials. The systems can be vacuum tight, allowing measurements to be conducted under vacuum or in an inert, reducing or oxidizing atmosphere. Data acquisition and evaluation, as well as instrument control, are carried out using a MS-Windows software package. The software allows the computation of the rate of mass change, mass change steps, onset and peak temperatures, inflection points, peak area integration, specific heat, etc. The combination of a NETZSCH thermobalance with a DTA or DSC measuring head makes up the simultaneous thermal analyzer. The mass change and the temperature difference are measured and, with enthalpy calibration of the DSC measuring head, the heat flow as well. The advantage is that both signals from the same sample are measured under exactly the same conditions at the same time. The simultaneous thermal analyzer provides all necessary electrical connections for the measurement signals, and the NETZSCH electronics (TASC) contains the appropriate amplifiers and analog - to - digital converters for transfer of the signals to the PC - compatible computer. The software is also designed to evaluate all measurement signals and graphically combines the various curves with their results.

### 3. Results and discussion

Density of samples was marked on the device Micrometric AccuPyc 1340 II Pycnometer. The results of measurements were presented on Table 1.

Samples were applied to delimitation of thermal conductivity about diameter 12.7 × 2.5 mm. It the sample after cleaning in ethanol, in the supersonic washer, was covered the thin layer of graphite to elimination of the phenomenon of radiational dissipation warm. Investigations were executed in the range of the temperature from 20 to 1400°C, in the vain line 10⁻⁵ mbar. Measurements were conducted in the isothermal mode, enlarging the temperature of the measurement gradually what 50°C to 400°C. More higher up the temperature was enlarged about 100°C, and three laser measurements (so - called “shots”) were executed for every temperature point. The examinations are shown on Figs. 6-11.

#### Table 1.

<table>
<thead>
<tr>
<th>Density powder for thermal barrier coatings</th>
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<tbody>
<tr>
<td>AMDRY 365C</td>
</tr>
<tr>
<td>6.0041</td>
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<tr>
<td>AMDRY 997</td>
</tr>
<tr>
<td>6.1325</td>
</tr>
<tr>
<td>METCO 45C NS</td>
</tr>
<tr>
<td>5.5831</td>
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<td>METCO 202 NS</td>
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<td>4.2200</td>
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<td>METCO 204 NS</td>
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<td>3.7686</td>
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**Fig. 5. STA 449 F3 Jupiter**

**Fig. 6. Thermal diffusivity of metallic powders for thermal barrier coatings**

**Fig. 7. Thermal conductivity of metallic powders for thermal barrier coatings**

**Fig. 8. Specific heat of metallic powders for thermal barrier coatings**

**Fig. 9. Thermal diffusivity ceramics powders for thermal barrier coatings**

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**Thermophysical properties of selected powders for thermal barrier coatings**
Fig. 10. Thermal conductivity of ceramics powders for thermal barrier coatings

Fig. 11. Specific heat of ceramics powders for thermal barrier coatings

4. Conclusions

The LFA method enables to measure of thermal conductivity of current used and developed materials for thermal barrier coatings. The using of combination of pycnometer, thermobalance and LFA system are the basic equipment for characterization of TBC’s properties. Thermal conductivity and thermal expansion coefficient are the factors, which decides about properties of TBC deposited by APS, LPPS and EB - PVD methods. The research presented in article showed the possibility of thermal properties measurement of real powders used in aerospace industry for TBC’s application.

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