Archives of Materials Science and Engineering

Volume 36
Issue 2
April 2009
Pages 76-81

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

Thermal diffusivity of $RE_2Zr_2O_7$ - type ceramic powders intended for TBCs deposited by APS

G. Moskal*, B. Witala, A. Rozmysłowska
Department of Materials Science, Silesian University of Technology,
ul. Krasińskiego 8, 40-019 Katowice, Poland
* Corresponding author: E-mail address: grzegorz.moskal@polsl.pl

Received 24.01.2009; published in revised form 01.04.2009

ABSTRACT

Purpose: The aim of this paper is to provide overall characteristics of the Laser-Flash method and to determine the thermal diffusivity of powders intended for thermal spraying of thermal barrier coatings (TBC) of new type by air plasma spray (APS). Lanthanum, samarium, neodymium and gadolinium zirconates based powders with a pyrochlore structure and a general formula $RE_2Zr_2O_7$ were used as the research material.

Design/methodology/approach: The scope of the study encompassed thermal diffusivity tests of zirconium powders with the laser-flash method using the Netzsch LFA 427 apparatus for direct measurement of diffusivity. The scope of measured temperature ranged from 25ºC to 1000 ºC (25, 250, 500, 750 and 1000°C). Every measurement point was repeated three times in order to obtain an average value.

Findings: The studies conducted have enabled determining the value of thermal diffusivity of the material analyzed in the form of powder within a wide range of temperature.

Research limitations/implications: The studies conducted suggest the necessity for verification of the obtained results for analogical coatings of the TBC type in order to determine the influence of the spraying process on the thermal diffusivity of the powders examined.

Practical implications: The research results obtained provide a basis for further research on the base material and in particular, on the influence of porosity on thermal diffusivity.

Originality/value: The original value presented in the paper is the information regarding the new type of ceramic materials intended for thermal spraying of TBCs.

Keywords: Metallic alloys; Thin&thick coatings; TBC; RE zirconates

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

G. Moskal, B. Witala, A. Rozmysłowska, Thermal diffusivity of $RE_2Zr_2O_7$ - type ceramic powders intended for TBCs deposited by APS, Archives of Materials Science and Engineering 36/2 (2009) 76-81.

MATERIALS

1. Characteristics of the Laser-Flash method

The Laser-Flash method was demonstrated for the first time by Parker, Butler, Jenkins and Abbott from the Military Laboratory of Radiological Defence in 1960. It belongs to the most popular methods of measuring temperature conduction of solid bodies and at the same time, it is the sole standardized method of measuring temperature conduction in transitory conditions. It is based on an analytical solution of Fourier's equation with adiabatic boundary conditions for an infinite flat sample exposed to Dirac's thermic impulse.

Its major advantages include:

- the easiness and efficiency of measurements,
- accuracy, credibility and reliability of results;
- applicability in a wide range of conditions and with reference to a wide range of metarials.

The most important assumptions of the LF method are the following:

- a sample is homogeneous and isotropic, with its thermophysical properties and density being invariable and constant, and they do not change with a change in temperature under the conditions of the study;
- the sample is thermally insulated; there are no thermal losses occur on the surface of the plate;
- a thermal impulse is uniformly distributed over the surface of the plate and absorbed by a layer of the material which is considerably thinner in comparison with the sample thickness;
- the thermal impulse is immediate and its duration is insignificant compared to the thermic reaction of the plate.

The basic equipment in the measuring apparatus used by the LF method consists of:

- a PC;
- a laser/xenon flash lamp;
- a thermographic detector of IR waves;
- an amplifier;
- a vacuum chamber;
- a control system.

The Laser Flash impulse method is based on measuring the heat flow recorded on the rear surface of the sample analyzed, the heat flow being the result of the laser impulse acting on the front side of the sample. From the physical perspective, this model of the method assumes the action of a heat source capable of emitting single impulses, e.g. a laser impulse acting onto one of the surfaces. An analysis of the heat flow onto the opposite side of the sample enables determining the required thermal properties. By assuming that the laser beam uniformly sweeps the front of the sample, a single-dimensional temperature gradient is generated, which may be thus described by means of a single-dimensional equation of heat diffusivity, the latter being the solution of Fourier equation [1,2].

2. Characterization of the LFA 427 apparatus by Netzsch

This apparatus consists of three systems (Fig.1):

Working part:

A base unit which enables safe operation under laser radiation, equipped with an integrated furnace and sensor system. It is also furnished with a sample carrier system and connectors to a vacuum pump, working gases and source of power supply. A general diagram of the system is presented in Figure 2.

In addition, it includes:

- a high-power Nd-YAG type laser of variable power 20J/p and a HeNe laser for positioning the sample carrier and optical elements;
- a sample carrier (from Al_2O_3/SiC) adapted to samples of a 12.7 mm diameter (Fig. 3);
- IR sensors cooled with liquid nitrogen with germanic filters;
- a high-temperature pipe furnace with a SiC heating element, an Al_2O_3 safety pipe, an integrated cooling system, control type S thermocouples. Working temperature 1500°C, max. temperature 1550°C (Fig. 4);
- a flow control system for the furnace water-cooling system with a rotational flowmeter, filters and piping.

Fig. 1. General view of the LFA 427 apparatus [3]

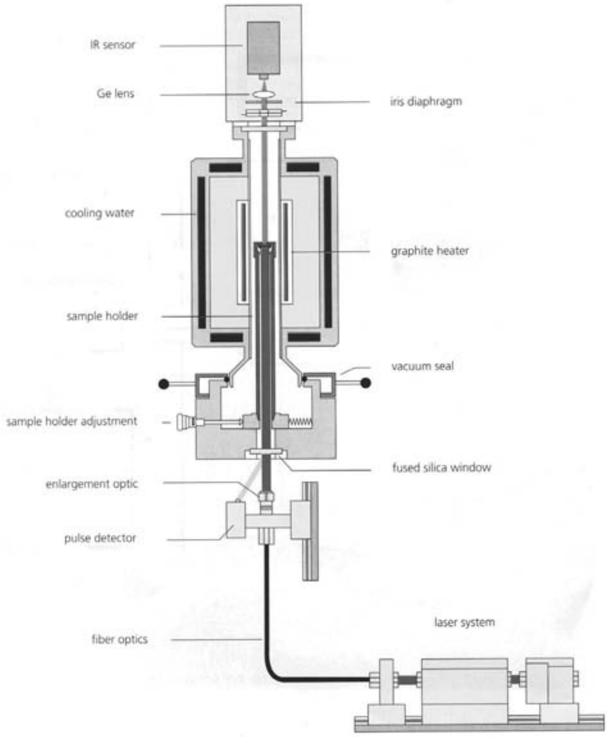

Fig. 2. Diagram of the working part of apparatus LFA 427 [3]

The entire measuring unit is constructed as a vertical system in the following order, upwards from the bottom: laser-sample-detector, without using mirrors on the laser beam route.

The source of radiation consists of a constant neodymium laser with the length of the emitted wave from the range of infrared radiation of 1064 nm and variable energy of up to 20J/impulse. The operating parameters of the laser, i.e. the energy and impulse length, are controlled at the software level, similarly to the shape of spot for each measurement.

The sample carrier system is distributed vertically (mounted at the bottom from the side of the laser, not underslung). Sample carriers, the so-called “holders” are adapted to mounting round samples, up to 12.7 mm in diameter and up to 6 mm thick, and performing measurements on them.

The apparatus has an option of its further equipping with sample carriers to enable measurement of liquids (e.g. water), fibre materials or slag. A diagram of such carrier is presented in Fig. 3.

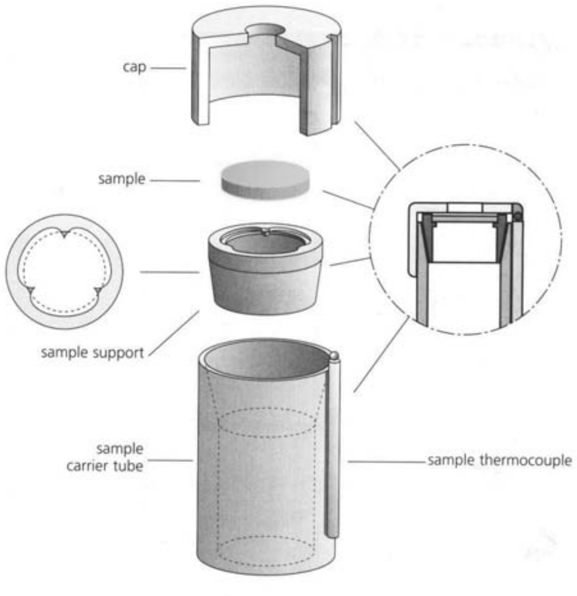

Fig. 3. Diagram of sample carrier [3]

The system is equipped with IR detectors cooled with liquid nitrogen. The detectors measure an increase of temperature on the non-heated part of a sample.

Another element of the system is the furnace ensuring maximum working temperature of approximately 1550°C. The furnace is cooled with water. and is equipped with a rotational vacuum pump to ensure obtaining maximum vacuum of min. $2x10^{-5}$ mbar. It also enables taking measurements in neutral, oxidizing and reduction atmospheres.

Additionally, the thermocouple system allows the determination of temperature inside the furnace as well as the temperature of the samples themselves. Temperature stability of a sample amounts to minimum +/-1.0 K at a prescribed value of temperature. The furnace is built in a modular system, which enables turning its easily into, e.g., a graphite furnace with a working temperature of up to 2000°C. By installing a nitrogen-based cooling system, it is possible to take measurements at a temperature of down to -70°C. A diagram of the furnace is presented in Fig. 4.

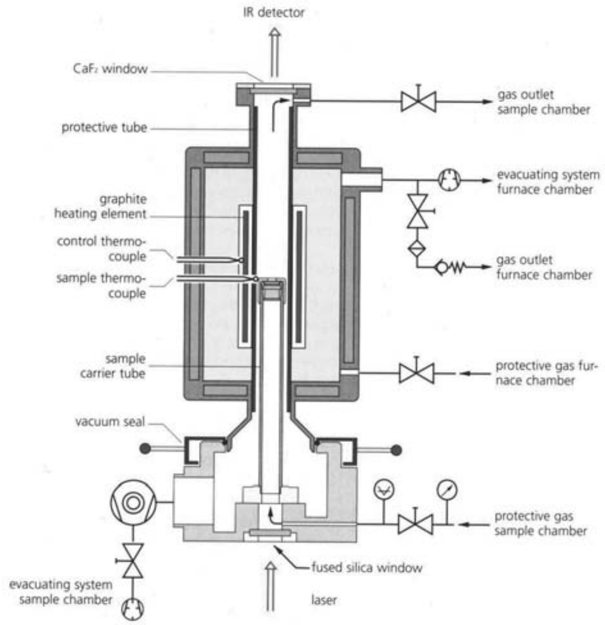

Fig. 4. Diagram of the furnace of apparatus LFA 427 [3]

Control/measurement part

This part consists of:

- A data acquisition system allowing the A/D converter sampling frequency of min. 500 kHz; it also enables recording of min. 10000 points for the detector signal and min. 2000 points for recording laser signals. Data collection proceeds at a speed of up to 0.002 ms;
- A temperature control and power supply system;
- Protection systems for power supply and for measurement sensors;
- A transformer;
- A casing of the system.

Software

The software enables full control of the equipment and supervision of setting the measurement parameters, control of performing the measurement, data acquisition and processing of measurement data. Furthermore, it enables data processing and analysis in digital and graphic forms. The analytical software includes a dozen or so various mathematical models for working out the measurement signals, as well as a mathematical model based on non-linear regression and an improved Cape-Lehman model taking into account front and radiation losses simultaneously. This software also contains a model for two- and three-layer materials, which enables characterizing the thermal properties of samples with protective coatings, e.g. of the TBC type. It also determines specific heat by means of a comparative method with an accuracy of 4%.

3. Measurement procedure

The operating principle of the apparatus, applied in this method, is described below. A sample is placed in the vacuum chamber of the furnace. This is where isothermal heating to a prescribed temperature takes place. Afterwards, a short laser impulse ”strikes” one side of the sample, as a result of which a temperature gradient is generated. This change is measured by an IR detector on the opposite surface of the sample. The results, collected by the recorder, are transmitted to a PC.

The temperature conduction is determined from a curve showing the change of temperature over time on the surface of the plate, the so-called thermogram and the sample thickness. The measurement procedure is presented in Fig. 5.

The conduction is calculated from the formula first presented by Parker:

$$a = 0{,}1388 \frac{g^2}{t_{0,5}} \tag{1}$$

where:
g – sample thickness;
$t_{0,5}$ – time in which the change of temperature on the second side of a sample achieves half of the maximum value.

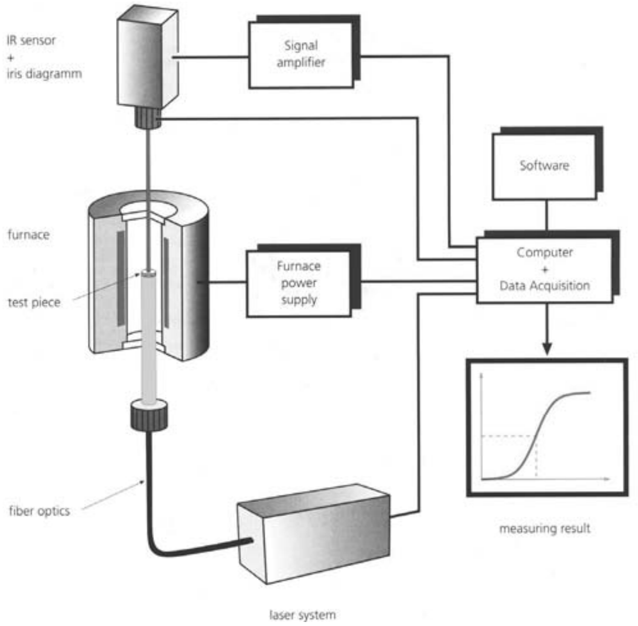

Fig. 5. Measurement procedure by the Laser Flash method using apparatus LFA 427 [3]

The apparatus allows the measurement of thermal diffusivity within the range from 0.001 to 10 cm^2/s with an accuracy higher than 3% in the scope from room temperature to 1500°C. It is also possible to determine specific heat. Appropriate software enables performing measurements for two-layer and three-layer systems.

4. Chemical and phases composition of $RE_2Zr_2O_7$ (RE – La, Gd, Sm, Nd) type of powder and thermal diffusivity characterization

The main material of the ceramic layer currently used in TBCs in zirconium oxide modified with yttrium oxide (YZS). It demonstrates numerous desirable properties [4], such as:

- high melting temperature of approx. 2700ºC;
- one of the lowest, among ceramic materials, thermal conductivity coefficients of the order of 2.3 $Wm^{-1}K^{-1}$, a decrease of the substrate surface temperature, an increase of working temperature and a reduction of thickness of the ceramic layer;
- a high coefficient of thermal expansion, 11×10^{-6} $ºC^{-1}$, which lowers the stresses resulting from differences in thermal expansion between the metallic base and ceramic coating;
- low density – 6.4 g/cm^3, which enables a reduction of the weight of turbine;
- a low elasticity modulus, E=50GPa, which enables reducing thermal stresses;
- high hardness of approx. 14GPA, which makes YSZ a material resistant to erosion and impacts.

Although the YSZ-based TBCs have been used for as long as 30 years now [5-10], their durability is still a considerable problem, which constraints their broader application [11-14].

The major issue consists in producing a ceramic material intended for the external layer of thermal coating barriers (applicable for both nickel- and niobium-based high-temperature creep resisting alloys), characterized by decreased conductivity as compared to YSZ, particularly in high temperatures. The new type of ceramic material should also exhibit chemical stability in contact with oxides, especially with Al_2O_3. Extensive research works are focused on this area, in particular on oxides of the $RE_2Zr_2O_7$ type, which are characterized by the following set of 6 desirable properties [15]:

- thermal conductivity lower than 2.0 $Wm^{-1}K^{-1}$;
- a linear coefficient of thermal expansion higher than 10×10^{-6} C^{o-1};
- maximum working temperature higher than 1600°C;
- Young’s modulus below 250GPa;
- hardness higher than 6GPa;
- density below $7g/cm^{-3}$.

When analysing a new type of ceramic material intended for thermal spraying with APS method, it is necessary to determine the following properties.

- characteristics of chemical and phase composition:
  - analysis of contents of gas oxygen and nitrogen;
  - analysis of contents of carbon and sulphur;
  - analysis of chemical composition;
  - quality analysis and quantity analysis of phase composition.

The first stage of testing involved analysis of chemical composition. Assessment of chemical composition by the OES-ICP method was carried out and this method proved inconsiderable quantity of additives and impurities, especially in a form of Si, Ti, Al, Y and Cu. Participation of these elements in all analysed cases was very similar. It showed that small quantities of sulphur and carbon are present in the powder as well (Table 1).

Table 1.
Results of analysis of chemical composition of analysed powders (OES-ICP)

Wt.%	$Gd_2Zr_2O_7$	$La_2Zr_2O_7$	$Nd_2Zr_2O_7$	$Sm_2Zr_2O_7$
Zr	28.5	30.6	28.9	29.8
Gd	59.7	-	-	-
La	-	59.1	-	-
Nd	-	-	58.9	-
Sm	-	-	-	60.0
Y	0.068	<0.01	<0.01	<0.01
Al	0.088	0.092	0.370	0.065
Si	<0.10	<0.10	<0.10	<0.10
Cu	<0.01	<0.01	<0.01	<0.01
Ti	<0.005	0.011	0.005	0.012
S	0.002	0.001	0.001	0.001
C	0.006	0.002	0.005	0.003

In order to get a precise assessment of phase composition, the XRD analysis of phase composition was carried out. In the case of gadolinium powder he presence of not only assumed $Gd_2Zr_2O_7$ phase, but also initial components in the form of Gd_2O_3 oxide and ZrO_2 oxide was found in the phase composition tests (Fig. 6). Intensity of oxide phase reflections shows to their relatively high volume fraction in the analysed material. In the other cases of zirconates. Results of XRD phases analysis of others powders are showed on Figs. 7 to 9.

The results of measurement of thermal diffusivity performed on the $La_2Zr_2O_7$, $Nd_2Zr_2O_7$, $Sm_2Zr_2O_7$ and $Gd_2Zr_2O_7$ powder sample are presented in Fig. 6. Measurements of thermal diffusivity of powders by a laser-flash method were carried out on round pressed samples (ϕ-12.7mm, h – 2mm). Samples in a state directly after pressing process were subjects of investigations with no other heating treatments. Neodymium powder (0,121 mm^2/s) has got the lowest value of diffusivity at ambient temperature and powder on samarium base has got the highest value of diffusivity (0.149 mm^2/s). A tendency to reduce diffusivity of all powders to temperature 750ºC and increase up to 1500ºC was noticed. Within a range of potential working temperature of the TBC layers, neodymium powder has got the best diffusivity and the other powders are ordered as following: lanthanum powder, samarium powder and gadolinium powder. Got values of diffusivity in temperature 1250 ºC are respectively as following: 0.097; 0.135; 0.146; 0.165 mm^2/s. Porosity of tested samples was below 1%.

5. Summary

- The studies conducted indicate that the value of thermal diffusivity of powder $RE_2Zr_2O_7$ (RE- La, Gd, Sm, Nd) fulfills the selection criteria for ceramic materials as coatings of the TBC type.
- The studies were conducted on a compact made of the La, Gd, Sm, Nd zirconates (pyrochlore structure) powder of negligible porosity and therefore, the result may be regarded as adequate for a solid material.

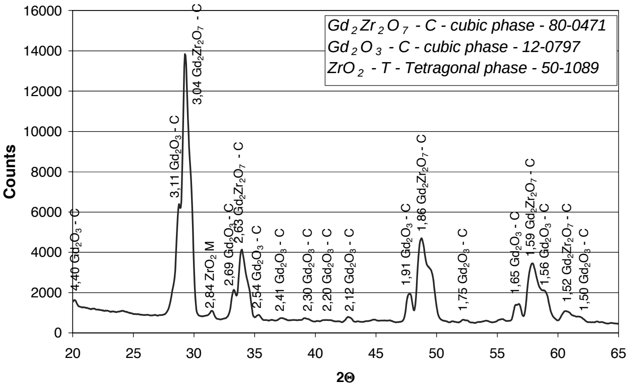

Fig. 6. X-ray diffraction pattern of the tested powder $Gd_2Zr_2O_7$ in initial state

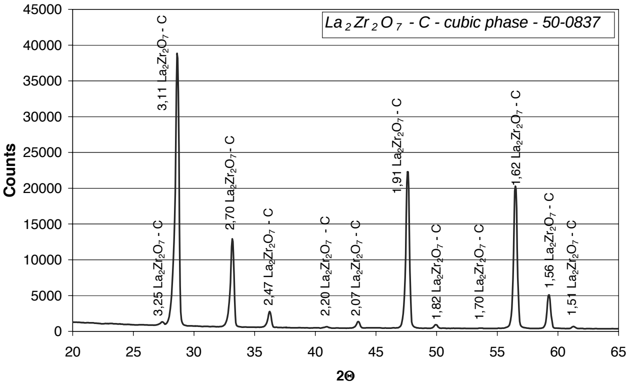

Fig. 7. X-ray diffraction pattern of the tested powder $La_2Zr_2O_7$ in initial state

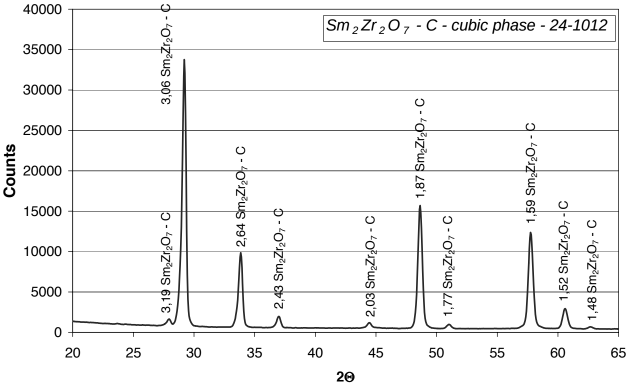

Fig. 8. X-ray diffraction pattern of the tested powder $Sm_2Zr_2O_7$ in initial state

- Thermal diffusivity of this material is at the level of no more than 0,15 mm^2/s at room temperature in the case of all types of powders and no mare than 0,12 mm^2/s in the case of highest temperature. The best insulating properties showed powder Nd zirconates type.
- A detailed analysis of thermal properties of the investigated zirconates powder requires additional research to determine the effect of porosity, temperature and sintering process on thermal diffusivity.

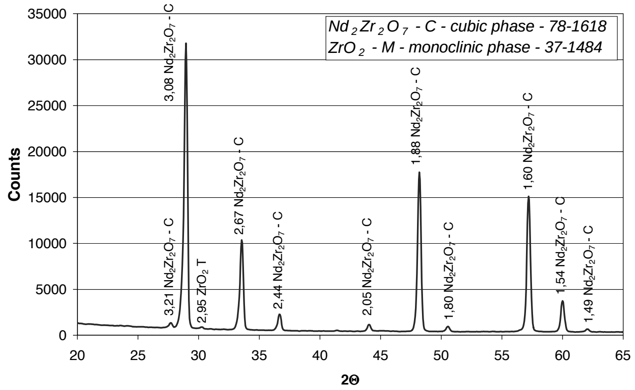

Fig. 9. X-ray diffraction pattern of the tested powder $Nd_2Zr_2O_7$ in initial state

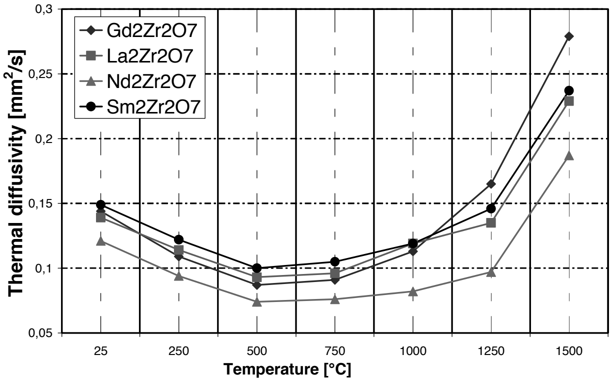

Fig. 10. Thermal diffusivity of powder $RE_2Zr_2O_7$ by L-F method

Acknowledgements

This work was supported by the Polish Ministry of Education and Science under the research project No PBZ-KBN-100/T08/2003.

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