Sensors and Actuators A 272 (2018) 42–52

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

On the thermal sensitivity and resolution of a YSZ:Er^{3+}/YSZ:Eu^{3+} fluorescent thermal history sensor

Stéphane Amiel*, Etienne Copin, Thierry Sentenac, Philippe Lours, Yannick Le Maoult

Institut Clément Ader (ICA), Université de Toulouse, CNRS, Mines Albi, UPS, INSA, ISAE-SUPAERO, Campus Jarlard, 81013 Albi CT Cedex 09, France

ARTICLE INFO

Article history:
Received 11 February 2017
Received in revised form 20 January 2018
Accepted 22 January 2018

Keywords:
Fluorescence
Thermal history sensor
Phosphor
Intensity ratio
Lifetime analysis
Thermal resolution

ABSTRACT

This paper deals with the problem of thermal history analysis of high temperature components for applications such as furnaces, nuclear reactors and jet engines. It focuses on fluorescent thermal history sensors, which exhibit permanent changes in their luminescence properties when exposed to high temperature. These changes can then be quantitatively evaluated to determine the temperature of exposure from a previous thermal event. The main objective of this paper is to investigate the thermal sensitivity and the thermal resolution of a yttria-stabilized zirconia (YSZ) Er^{3+}-doped phosphor produced by a sol-gel route and combined with a thermal history insensitive YSZ:Eu^{3+} reference, which was selected for its high sensitivity to thermal history above 1173 K. In particular, the interest of this YSZ:Er^{3+}/YSZ:Eu^{3+} sensor is discussed in the view of the physical properties of sol-gel deposited YSZ coatings, the selection of an appropriate excitation wavelength and the practical measurement of coatings fluorescence properties. The sensitivity and the resolution of two thermal history measurement fluorescence methods, based on intensity ratios and lifetime analysis, were determined and compared. A comparison is also made with standard non-contact temperature measurement methods such as infrared thermography and thermochromic paints.

1. Introduction

For many industrial processes in energy [1], aeronautical [2], automobile engineering [3] or in microelectronics [4], temperature is a key parameter for their design, for their control and for the durability of their associated components. However, temperature measurement under high heat-flux conditions and in confined environments such as furnaces, nuclear reactors and aircraft jet engines remains challenging. In particular, the use of standard on-line measurement methods (thermocouples [4], IR thermography methods [5–7], etc.) is sometimes not appropriate in harsh environments involving limited optical access and fast- moving components such as jet turbine engines [8]. Such environments require robust, reliable and non-intrusive sensors that can be used with the relevant component surface. Some type of sensors, called thermal history sensors, have the ability to record the temperature to which they are exposed during a thermal event so that annealing temperatures can be extracted from a later off-line analysis at room temperature.

The most widely-used thermal history sensors are thermochromic paints [9], which exhibit permanent changes of colour with temperature and duration of exposure. These paints are for instance used for off-line temperature determination on coated parts after running a test engine in a predefined cycle [10–12]. However, the thermal resolution of such temperature-sensitive paints, which relies on the number of their discrete colour changes, varies between 10 K and more than 100 K [9]. Furthermore, some substances present in the pigments are now restricted by European Union REACH regulations.

This context has led to the development of a new alternative class of thermal history sensors, based on temperature-driven changes in the emission properties of fluorescent markers embedded within a coating [13,14]. These markers, or phosphors, are made up of an inorganic matrix containing luminescent centres, typically trivalent lanthanide ions, which have the ability to emit photons when excited at an appropriate wavelength, as a result of radiative electronic transitions. For short-time exposure to high temperature, the temperature-induced physicochemical changes occurring within a phosphor at the atomic scale can permanently modify the electronic structure of the activator ions and the radiative electronic transition probabilities, hence causing permanent changes in the spectral (wavelength and intensity) and temporal (decay time) fluorescence emission properties. The off-line analy-

* Corresponding author.
E-mail address: stephane.amiel@laposte.net (S. Amiel).

https://doi.org/10.1016/j.sna.2018.01.040
0924-4247/

sis at room temperature of its fluorescent properties can thus reveal the peak temperature undergone by the fluorescent sensor under stationary annealing conditions. Changes in the fluorescence characteristics have an advantage over colour changes, in that they are continuous and readily measurable quantitatively using standard spectroscopic equipment, making it possible to measure a continuous spectrum of temperature rather than temperature thresholds.

Currently, crystal phase transition process [15], enhancement of crystallinity [13,14,16,17], oxidation of activator ions [18,19] and diffusion of activator or sensitizer/quencher species [14,20] are the four main thermoactivated mechanisms identified in fluorescent thermal history sensors which can cause a temperature sensitivity appropriate for thermal history sensing. Phase transitions between allotropic forms of Mn^{2+} doped $Zn_3(PO_4)_2$, synthesized by Salek et al. [15] caused strong changes in its fluorescence emission chromaticity in the range 873 K–1273 K, making it suitable for recording thermal history. Gonzàlez et al. [18,19,21] observed that the process of oxidation from Eu^{2+} to Eu^{3+} in a $BaMgAl_{10}O_{17}$ is temperature-sensitive up to 1673 K. The emission ratio built from the 445 nm and 611 nm emission lines of Eu^{2+} and Eu^{3+} ions after a 20 min-long isothermal heat treatment exhibited a threefold order of magnitude increase from 973 K to 1373 K, with repeatability of the ratio better than 10 K. On the same principle, Rabhiou et al. [18], from the same team, observed that the phosphor $SrAl_{14}O_{25}:Eu^{2+/3+}$ could provide a dynamic range extending from 873 to 1573 K. The same authors also demonstrated that an amorphous-to-crystalline transition in sol-gel synthesized $Y_2SiO_5:Tb^{3+}$ after 20 min-long heat treatments causes a monotonic increase in fluorescence intensity and decay time over a temperature range from 773 K up to 1073 K, which also makes this phosphor suitable for thermal history sensing [14,16,18]. The accuracy of these phosphors, when put in suspension in a commercial binder and painted on a disk submitted to the flame of a burner for 40 min was estimated to be better than 50 K [16]. A water-based paint containing an amorphous Eu doped matrix developed by the same team also showed monotonic variation in its decay time within the temperature range 373–1073 K, with excellent repeatability. Finally, other thermal history sensor coatings for high temperature based on the enhancement of crystallinity were also reported by Pilgrim et al. [22] (Eu^{3+} and Dy^{3+} doped YAG, 573 K–1073 K) and Stenders et al. [23] (Eu^{3+}/Tb^{3+} doped Y_2O_3, 973 K–1273 K).

Over the last few years, the Institut Clément Ader has been developing YSZ phosphors and coatings prepared by a sol-gel route for high temperature sensing in thermal barrier coatings, such as YSZ:Eu^{3+} and YSZ:Er^{3+} [24–26]. In particular, the latter was found to be a suitable candidate for thermal history sensing [27]: the continuous enhancement of crystallinity of YSZ:Er^{3+} powders produced by a sol-gel route with temperature for 15 min long heat treatments between 1173 K and 1423 K induced substantial and consistent increases of their green emission intensity and fluorescence decay time in the ranges 1223 K–1423 K and 1173 K–1373 K respectively [27]. As shown in Fig. 1, the intensity of the main emission lines at 540 nm and 560 nm were indeed observed to increase with crystallinity by a factor of almost 50 after 15 min at 1423 K. These strong temperature dependencies could allow off-line temperature sensing with an estimated theoretical resolution for those temperatures ranging between 0.3 and 1 K and between 6 and 2 K for intensity and decay time respectively, surpassing the resolution of actual thermochromic paints in that temperature range. Preliminary investigations confirmed the potential of an intensity ratio approach, using a red emitting, temperature insensitive YSZ:Eu^{3+} reference (Fig. 1), as a robust method regarding small variations in experimental measurement conditions for future applications in off-line temperature mapping. Furthermore, the stability of the thermal exposure temperature sensing capability for relatively long time heat treatments below 973 K that was observed is expected

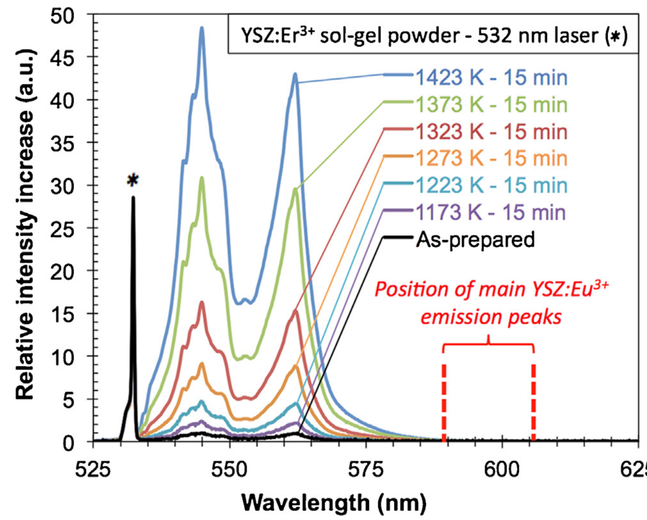

Fig. 1. Evolution of the relative intensity increase of the fluorescence emission of a sol-gel synthesized YSZ:Er^{3+} powder with the temperature of exposure after 15 min long heat treatments [27]. The position of the main emission peaks of YSZ:Eu^{3+}, which could be used as a reference because of its little sensitivity to temperature of exposure when fully crystallized, is also indicated.

to allow to directly co-deposit these two YSZ:Eu^{3+} and YSZ:Er^{3+} phosphors as a thermal history sensing coating using sol-gel deposition methods such as air-spraying followed by a low temperature consolidation heat treatment (<973 K).

This paper aims to provide a more in-depth analysis of this fluorescent YSZ:Er^{3+} thermal history sensor, in regards with its practical application in the form of a coating deposited by a sol-gel process in combination with a thermal history insensitive YSZ:Eu^{3+} reference. In particular, the interest of this YSZ:Er^{3+}/YSZ:Eu^{3+} coating is discussed in the view of the physical properties of sol-gel deposited YSZ coatings, the selection of an appropriate excitation wavelength and the practical measurement of coatings fluorescence properties. The sensitivity and the resolution of a hybrid YSZ:Er^{3+}/YSZ:Eu^{3+} phosphor for both an intensity ratio and lifetime analysis based approaches, determined from temperature calibration curves from earlier work [27], are investigated and compared with standard methods for measuring temperature.

2. Experimentation

2.1. Preparation of YSZ: Eu and YSZ: Er phosphor and coatings

YSZ:Er^{3+} powder of composition $(YO_{1.5})_{0.083}(ErO_{1.5})_{0.015}(ZrO_2)_{0.902}$ and YSZ :Eu^{3+} powder of composition $(YO_{1.5})_{0.078}(EuO_{1.5})_{0.02}(ZrO_2)_{0.902}$ were synthesized by a sol-gel route using the protocol described in reference [27]. Samples of the YSZ:Er^{3+} powder, in a partially crystalline state after calcination at 973 K for two hours, were further annealed for 15 min under isothermal conditions at various temperature between 1173 K and 1423 K with 50 K steps. During these heat treatments, the samples were introduced in the furnace already set at the intended temperature and were removed after 15 min and let for cooling in open air, in order to recreate conditions of thermal history sensing close to that of real applications of thermochromic paints (3–5 min) [10–12].

The YSZ:Eu^{3+} powder, also in a partially crystalline state after calcination at 973 K for two hours, was simply annealed for 2 h at 1373 K to ensure full crystallization [27], as this phosphor was selected to play the role of a reference with little sensitivity of its fluorescence emission properties to thermal history when further calcined for 15 min between 1173 K and 1423 K.