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Phosphor Thermometry of Alumina-Forming High-Temperature Alloys Using Luminescent Rare-Earth Ions in YAG: Proof of Concept Using a Dispersion of Ce^{3+} -Doped YAG Particles in a FeCrAl Alloy

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Most high-temperature processes require monitoring and controlling temperature, preferably with high precision and good lateral resolution. Here we evaluate the use of the technique commonly known as phosphor thermometry, which exploits the temperature dependent photoluminescence from an inorganic phosphor, for the determination of the temperature of a composite material consisting of the metallic alloy FeCrAl dispersed with phosphor particles of yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) doped with a small amount of luminescent Ce^{3+} ions (YAG:Ce^{3+}). The results show that with some optimization and by changing the dopant ion, YAG based phosphor particles offer a unique opportunity to measure the surface temperature of metal alloys with high precision and high lateral resolution, all the way up to the maximum working temperature of alumina-forming high temperature alloys at ca. 1300 °C.

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The iron-based, bcc-structured and alumina-forming FeCrAl alloys is an important class of high-temperature alloys having excellent oxidation properties and corrosion resistance.[1] FeCrAl alloys are used up to 1300 ˚C in air as resistive heating elements and in many other high temperature applications such as radiant tubes in furnaces, shielding tubes, furnace furniture and construction components, and high temperature petrochemical processes.[2] The ability of FeCrAl alloys to resist high temperature oxidation and corrosion relies on the spontaneous formation of a continuous and adherent Al_2O_3 layer on the surface.[3,4] The surface alumina layer protects the alloy because it grows slowly and forms a barrier towards other reactants in the environment, such as nitrogen and carbon, that could otherwise react with and destroy the alloy.[5]

Controlling and monitoring the temperature is a basic requirement for all high temperature processes and applications. Besides the need to control and regulate process temperature, the properties and ageing of the process equipment also depends on temperature. Indeed, the ability to control temperature can determine the useful life of components and can be decisive for the viability of equipment, engines, processes, and entire technologies.

Conventionally, the working temperature of a high temperature component is measured by thermocouples or pyrometry. However, thermocouples are not useful with moving components and pyrometry only provides moderate precision and both methods have limitations when it comes to lateral resolution. Phosphor thermometry is an alternative way to measure temperature which addresses some of these challenges.[6] The technique is based on the thermal dependence of the photoluminescence (PL) of inorganic phosphors and provides a contact-free, precise, and non-destructive way of temperature determination. For example, J. Feist and his team designed a system based on phosphor thermometry and showed that it can be used to determine the thermal history of components exposed to high temperature environments such as engines, fuel cells, furnaces, etc.[7] In their system they used yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) doped with a rare earth element (Ce, La, Pr, Yb, etc.) as luminescent ions.

In this work we report on the preparation, characterization, and luminescence properties of a composite material consisting of FeCrAl alloy containing a dispersion of YAG particles doped with a small amount of luminescent Ce^{3+} ions (YAG:Ce^{3+}). The aim is to evaluate the capability and capacity of using YAG:Ce^{3+} particles in FeCrAl alloys to probe the surface temperature of these materials. To work as a temperature probe, the particles must be compatible both with the alloy matrix and with the protective alumina scale. The rationale for choosing YAG as the host crystal rather than other refractory oxides, is related to its high thermodynamic stability. Thus, YAG:Ce^{3+} is not expected to react with the components of the alloy matrix. Moreover, it is noted that all commercial alumina-forming high temperature alloys, including the FeCrAl:s, are added with small amounts (<0.1% by weight) of elemental yttrium (together with additional so-called reactive elements, RE:s), mainly to enhance the adhesion of the protective alumina scale.[8] Upon exposure to oxygen-containing gases at high temperature, yttrium which is present at the alloy surface becomes fully oxidized, forming Y^{3+} ions which become incorporated into the alumina scale. With time, Y^{3+} in the scale forms YAG which is thermodynamically the most stable compound of Y^{3+} in an alumina environment.[8] Hence, YAG particles are also expected to be compatible with the alumina scale, implying that YAG:Ce^{3+} particles (and indeed any phosphor consisting of YAG doped with a rare-earth ion) at the alloy surface will not change its properties, meaning that it may serve as a reliable temperature probe throughout the life of a FeCrAl component.

YAG:Ce^{3+} Characteristics

The YAG:Ce^{3+} crystal structure may be viewed as a network of {Y,Ce}O_8 dodecahedra, AlO_6 octahedra, and AlO_4 tetrahedra, which are connected to each other via O atoms that are shared between neighbouring cation-oxygen polyhedra.[9] YAG:Ce^{3+} phosphor shows a bright yellow-green emission in the 500–700 nm range, due to electronic $5d \rightarrow 4f$ transitions, upon excitation with a blue light source.[10] Crucially, YAG:Ce^{3+}, as well as other inorganic phosphors, exhibit a pronounced, reversible, reduction of the PL emission at elevated temperature.[10,11] This phenomenon is known as *thermal quenching of luminescence* and is, for most applications, such as in lighting, an unwanted but unavoidable behavior. However, as of specific concern here, the thermal quenching of luminescence may be exploited for temperature determination.

Experimental

Sample preparation.—The alloy/YAG composite was supplied by Kanthal AB. It was prepared by hot isostatic pressing (HIP:ing) of a powder mixture consisting of 95 weight% of alloy Kanthal® APMT and 5 weight% of YAG:Ce^{3+}. The concentration of Ce^{3+} in YAG:Ce^{3+} was 3.33 mol%, i.e. the $Ce^{3+}/(Y^{3+} + Ce^{3+})$

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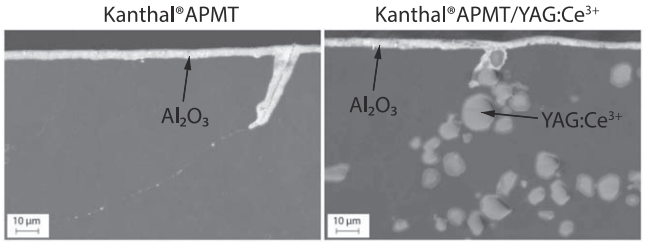

Figure 1. SEM cross section images after 168 h exposure to air at 1100 °C. The image to the left shows the Kanthal®APMT alloy while the right-hand image shows the Kanthal®APMT /YAG:Ce^{3+} composite material.

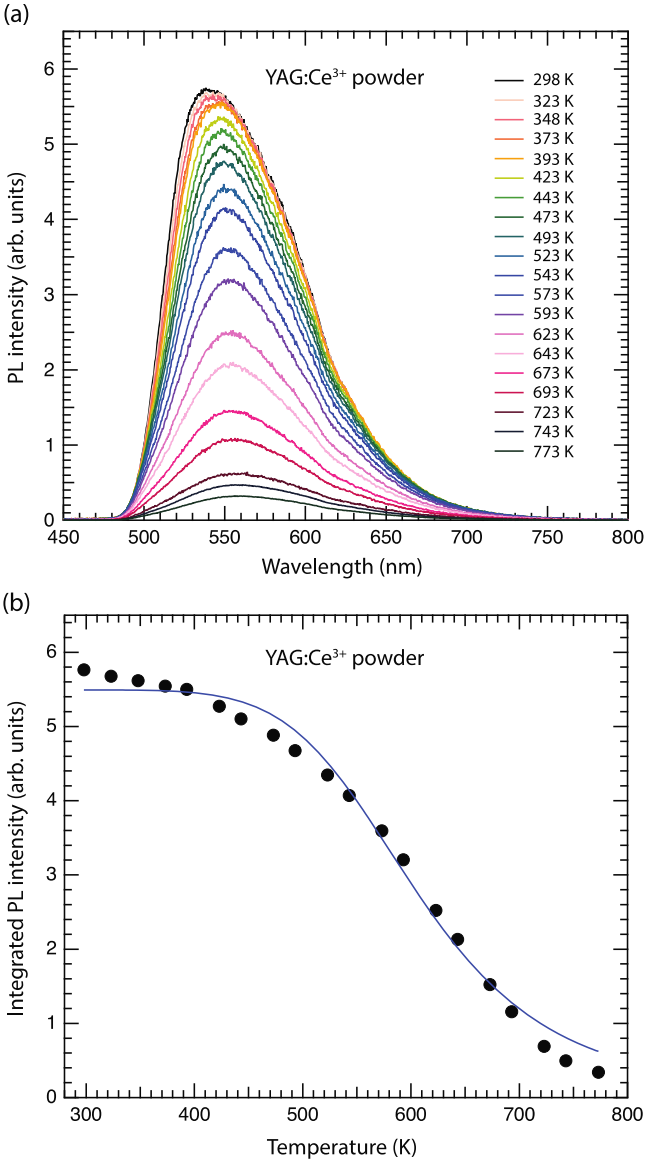

Figure 2. Variable temperature PL spectra (a) and integrated PL intensity (b) of YAG:Ce^{3+} powder under excitation at 450 nm. The line is a fit to a single barrier quenching model, and corresponds to a thermal quenching temperature of 606 K.

concentration ratio was 3.33 mol%. The YAG:Ce^{3+} phosphor (branded HTY550) was purchased from PhosphorTech Corporation. The powder mixture was placed inside a steel capsule and subjected to HIP:ing at 1150 ˚C for 8 h. The resulting Kanthal®APMT/YAG:Ce^{3+} composite slab was cut into sample coupons with a dimension of 10 × 10 × 1.0 mm. The coupons were prepared by grinding and polishing before the experiments. The sample faces were polished with 1 μm diamond paste, producing a mirror-like finish, and the sample edges were ground using 1,000# mesh SiC paper. Lastly, the coupons were carefully cleaned in an ultrasonic bath in two steps, first in acetone, then in ethanol.

In order to form an α-Al_2O_3 layer on the surface of the Kanthal®APMT/YAG:Ce^{3+} composite, the samples were heated to 1100 ˚C in air for 168 h.

Scanning electron microscopy.—Scanning electron microscopy (SEM) images were recorded using a Zeiss Ultra 55 FEG-SEM, in order to check the morphology of the sample before and after high temperature treatment. Cross-sectional samples were prepared by broad ion beam milling using a Leica TIC3X ion beam milling system. Imaging was performed in secondary electron mode using an acceleration voltage of 20 kV to provide a good contrast between the alumina scale, YAG-particles and the metal matrix.

Photoluminescence measurements.—To measure the thermal quenching of luminescence, the samples were excited at 450 nm using a pulsed laser (DeltaDiode-450L from HORIBA Scientific) and the luminescence signal was collected using an optical fiber and guided to a detector using an Ocean Optics USB 2000+ UV–vis spectrometer. The measurements were performed on Kanthal®APMT/YAG:Ce^{3+} composite samples and, for reference, on YAG:Ce^{3+} powder, in the temperature range of 300–800 K. Elevated temperatures were reached with a Linkam THMS600 temperature control stage.

Results and Discussion

Figure 1 shows SEM images of Kanthal®APMT and of the Kanthal®APMT/YAG:Ce^{3+} composite, both after 168 h exposure to air at 1100 °C. The exposure to air resulted in a mass gain of 0.75 (±0.04) mg.cm^{-2}, due to the formation of a 4.0 μm thick alumina surface layer (bright contrast), for both Kanthal®APMT and the Kanthal®APMT/YAG:Ce^{3+} composite. Thus, the kinetics of alumina scale growth on the alloy and on the composite have been similar.

The SEM image of Kanthal®APMT reveals an oxide "peg", extending 20–30 μm into the material which appears to follow a grain boundary in the alloy. The image of the composite material shows that the YAG:Ce^{3+} particles (light grey contrast) are distributed throughout the alloy matrix. The particle size is in the 2–10 μm range and there is some tendency for agglomeration. The particle/matrix interfaces appear to be free from voids and no indication of YAG/alloy reaction was detected.

The different coefficients of thermal expansion (CTE) of the YAG:Ce^{3+} particles and of the alloy matrix (about 7.10^{-6}/K[12] and 13.10^{-6}/K,[13] respectively, at 1000 K) will tend to generate mechanical stresses in the composite in the as-synthesized condition as well as during cooling after the exposure at 1100 °C. Thus, during the PL measurements the particles are expected to be under compression while the alloy matrix will be under tensile stress. Note that one of the YAG:Ce^{3+} particles close to the surface is surrounded by alumina which has grown into the alloy matrix. The penetration of alumina along the particle/matrix interface may be related to the CTE mismatch. Locally enhanced inward growth of the alumina surface layer, as evidenced in the present case both by Kanthal®APMT and by the Kanthal®APMT/YAG:Ce^{3+} composite, is frequently reported for FeCrAl(RE) alloys at high temperature.[14] It is noted that the CTE mismatch may have deleterious effects on the ability of the composite to withstand oxidation under thermal cycling.

Figure 2a shows variable temperature PL emission spectra of YAG:Ce^{3+} powder under excitation at 450 nm. In full agreement with the literature, YAG:Ce^{3+} exhibits strong PL in the 500–700 nm range and the PL exhibits a systematic decrease in intensity with increasing temperature from 298 K to 773 K.[11,15] For a quantitative determination of the thermal-quenching behavior we consider the thermal quenching temperature $TQ_{50\%}$, which is defined here as the

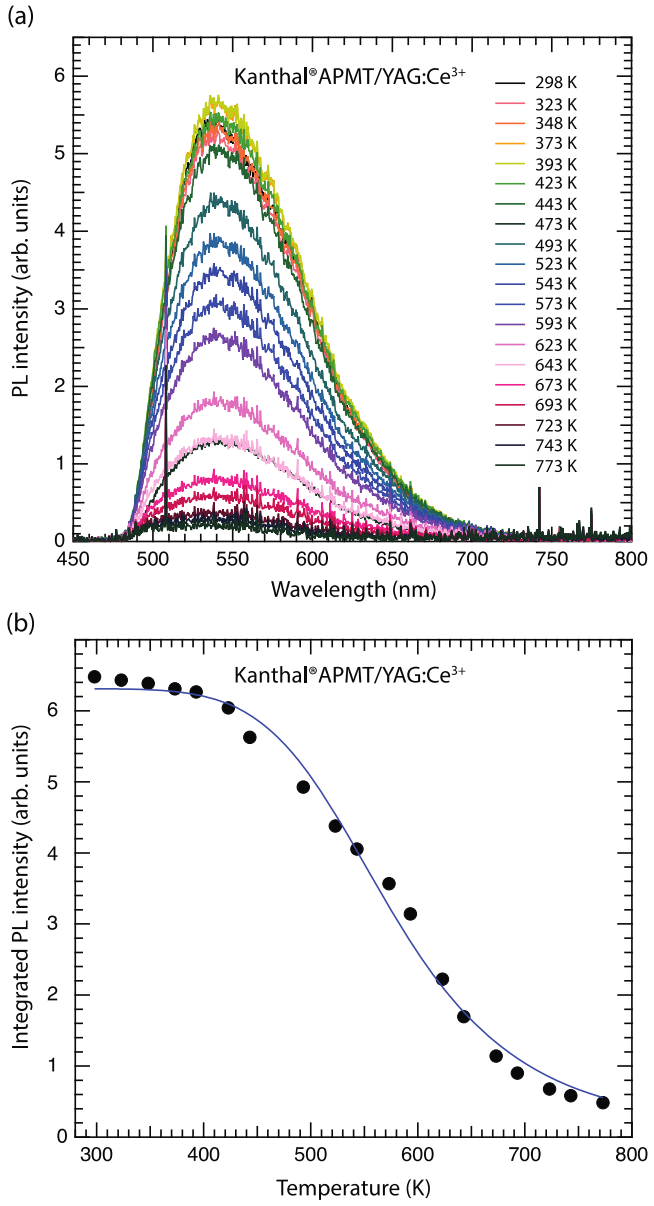

Figure 3. Variable temperature PL spectra (a) and integrated PL intensity (b) of Kanthal®APMT/YAG:Ce^{3+} composite under excitation at 450 nm. The line is a fit to a single barrier quenching model, and corresponds to a thermal quenching temperature of 576 K.

temperature at which the integrated PL intensity has dropped to 50% of its low-temperature (298 K) value. Figure 2b shows the temperature dependence of the PL intensity integrated over the spectral range of 450–800 nm. The data have been approximated with a single-barrier quenching model (blue line) with $TQ_{50\%} = 606(\pm10)$ K, in fair agreement with the literature that reports values in the range of 525–577 K for YAG:Ce^{3+} phosphor with a Ce^{3+} dopant concentration of 3 mol%.[15] The variation of $TQ_{50\%}$ amongst different studies may be an effect of small differences in local structural properties of different YAG:Ce^{3+} powder samples, as the thermal quenching of luminescence depends crucially on the presence and concentration of defects in the material.[15]

Figure 3a shows variable temperature PL emission spectra of the Kanthal®APMT/YAG:Ce^{3+} composite under excitation at 450 nm, whereas Fig. 3b shows the temperature dependence of the corresponding integrated PL intensity. The data in Fig. 3b can be adequately approximated with a single-barrier quenching model (blue line) with $TQ_{50\%} = 576(\pm10)$ K. What causes the difference between the thermal quenching temperature of the Kanthal®APMT/YAG:Ce^{3+} composite and YAG:Ce^{3+} powder is at present not clear. Nevertheless, it is important to note that the shape of the PL spectra for Kanthal®APMT/YAG:Ce^{3+} and YAG:Ce^{3+} are similar, cf. Fig. 3a and Fig. 2a. This shows that the PL properties of YAG:Ce^{3+} are not, at least not significantly, altered when incorporated into the alloy matrix. Yet, the PL signal is only about 1% of that for YAG:Ce^{3+}. This decrease in PL intensity is attributed to the combined effect of (i) the presence of the alumina surface layer (Fig. 1), which may scatter both the incident and emitted light, and (ii) the fact that YAG:Ce^{3+} only makes up a small fraction of the surface of the composite. Crucially, however, our analysis shows that the surface temperature of the sample can be measured up to, at least, 500 °C, which thus constitutes a proof-of-concept for exploiting YAG:Ce^{3+} phosphor particles as an internal temperature probe for Kanthal®APMT and likely also for other types of alumina-forming high temperature alloys. In this context, we believe that by replacing Ce^{3+} with other dopant ions as well as by improving the sensitivity of the measurement setup, we will be able to measure the surface temperature of metal alloys in actual applications, with high precision, and high lateral resolution. In fact, it has been shown that YAG doped with Dy^{3+} and Tm^{3+} exhibits luminescence all the way up to 1700 °C.[16,17] This suggests that similar dispersions of YAG-based phosphors in metal alloys may be used to measure temperatures up to the maximum working temperature of alumina-forming high temperature alloys at ca. 1300 °C.

Finally, we note that the concept of luminescence thermal quenching is capable of high precision temperature measurements (±1 °C), provided that the measurement setup is optimized. Achieving precise temperature measurements requires a highly stable optical detector and a more optimized optical path than in the present case. By applying a small excitation spot and using a micro-luminescence setup it may even be possible to measure the luminescence signal of individual YAG:Ce^{3+} particles in the composite.

Conclusions

Our results show that YAG:Ce^{3+} phosphor particles dispersed in the high temperature alloy Kanthal®APMT can be used as an internal temperature probe. With some optimization and by changing the dopant ion, YAG-based phosphor particle dispersions in alumina-forming high temperature alloys can measure the alloy's surface temperature with high precision and high lateral resolution and up to the maximum working temperature of the alloys at 1300 °C.

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