Effect of Adding MgO_2 to a Selection of Resbond® Thermally Sensitive Paints

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For many years, phosphor thermometry has been used for non-contact measurements in hostile high temperature environments, which can include large blackbody radiation backgrounds, vibration, rotation, fire/flame, pressure, or noise. Often these environments restrict the use of thermocouples or infrared thermometric techniques. In particular, temperature measurements inside jet turbines, rocket engines, or similar devices are especially amenable to fluorescence techniques. Often the fluorescent materials are used as powders, either suspended in binders and applied like paint or applied as high temperature sprays. These coatings will quickly assume the same temperature as the surface to which they are applied. The temperature dependence of fluorescent materials is a function of the base matrix atoms and a small quantity of added activator or "dopant" ions. Often for high temperature applications, the selected materials are refractory and include rare earth ions. Phosphors like $Y_3Al_5O_{12}$ (YAG) doped with Eu, Dy, or Tm, Y_2O_3 doped with Eu, or similar rare earth compounds, will survive high temperatures and can be configured to emit light that changes rapidly in lifetime and intensity. For example, fluorescence from YAG:Dy was recently observed at 1,700 ºC at Oak Ridge National Laboratory (ORNL) in Tennessee. Recent research has shown that Cotronics Resbond ceramic binders can survive up to 1500 ^{o}C in temperature sensitive paint (TSP) configurations. It is hoped that the addition of magnesium oxide (MgO_2) will cause the TSP to more quickly assume the temperature of the substrate and reduce thermal shock, which reduces the useful life of the coating. Preliminary testing shows that for this particular series of binders the addition does not improve the survivability of the coating.

Introduction

Phosphors are fine powders that are doped with trace elements that give off visible light when suitably excited. Many of these phosphors have a ceramic base and can survive and function at high temperatures such as those present during combustion. When the phosphor is applied as a thin coating, it quickly equilibrates to the ambient environment and can be used to measure the surface temperature.

The basic physics of thermographic phosphors is well established, and researchers at Oak Ridge National Laboratory (ORNL) have demonstrated several useful applications [ref. 1-11]. The thermometry method relies on measuring the rate of decay of the fluorescence yield as a function of temperature. Having calibrated the phosphor over the desired temperature range, a small surface deposit is excited with a pulsed laser. The resulting fluorescent decay (typically in less than 1 ms) time is measured to calculate the temperature of the substrate. In many instances, (e.g., in a continuous steel galvanneal process) a simple puff of powder onto the surface provides an adequate fluorescence signal [ref. 1-2].

Research completed at ORNL during the summer of 2003 provided basic results as to which Cotronics® Resbond temperature sensitive paint (TSP) formulations emitted fluorescence and remain mechanically viable at high temperatures [ref. 12]. The tested 791, 792, 793, and 795 Resbond® ceramic binders were manufactured by Coltronics Corporation of Brooklyn, New York. These results show that all of the tested Resbond-based TSPs showed some fluorescence after thermal cycling to 1300 °C. Fluorescence was also observed for all but one TSP sample at 1400 °C. Only three TSPs, made with Resbond 792 and 793, showed significant fluorescence at 1500 °C. Fluorescence was observed at 1600 °C for one TSP containing Resbond 793. These results are consistent with similar survivability measurements completed with other TSPs. In addition, Resbond 793 appears to have the best TSP characteristics of the Cotronics binders, and it is one of the few binders that survives above 1500 °C. This research was completed as part of a three-year program funded by the NASA John H. Glenn Research Center in Cleveland, Ohio.

During the final phases of the NASA-Glenn research, it was hoped that the addition of magnesium oxide (MgO_2) would help selected TSP paints to more quickly assume the temperature of the substrate. This paper will give an overview into research designed to evaluate the effect of adding MgO_2 to selected TSPs. Emphasis will be placed on developing procedures and techniques for the application and the pre-treatment of candidate binder and phosphor combinations.

Binders

For this research, several Cotronics Resbond® ceramic binders were evaluated with MgO_2 and a powdered Y_2O_3:Eu phosphor. The main fluorescence emission from Y_2O_3:Eu occurs at a wavelength of 611 nm. Selected material and preparation properties for the tested Cotronics binders are given in Table 1. The Resbond series of ceramic binders includes six different formulations. Of these, only the three formulations listed in Table 1 were tested with MgO_2.

Sample Preparation

In order to create the TSPs, phosphor powder is mixed with ceramic binder. The compositions for paint samples used in this research are shown in Table 2. Typically, the phosphor powder account for twenty percent by volume of paint mixture. Ten percent by volume of a magnesium oxide was added to the mixture displacing the binder. This addition was an attempt to increase the thermal conductivity, reduce the thermal shock, and increase the survivability of the coating.

Table 1. Properties for selected Cotronics Resbond® ceramic binders.

Resbond Composition	791 Silicate Glass	792 Silicate Glass	793 Silica Oxide
Applications	Adhesives Coatings	Adhesives Coatings Electronics	Bonds Fibrous Materials
pH	Mildly Basic	Mildly Basic	Mildly Basic
Maximum Temperature (°C)	1650	1650	1760
Density (g/cm^3)	1.40	1.20	1.42
Viscosity (cps)	1500	150	50
Cure Time (hours)	24	24	24
Cycling Instructions	16 hours 25 °C or 2 hours at 120 °C	16 hours 25 °C or 2 hours at 120 °C	2 hours 25 °C or 2 hours at 175 °C

The paint preparation procedure began by measuring the powdered solids in a graduated capped vial. Individual tubes were vibrated to insure proper volume. Liquids were then added in predetermined amounts. After all the components were added to the cylinder, they are mixed by vigorously shaking the capped vial. The mixture was applied to the surface of a cleaned alumina substrate using a commercial airbrush. The TSPs were allowed to cure according to the manufacturer's specifications as shown in Table 1. In the case of Resbond 791, water was added to thin the mixture to make it easier to apply using the airbrush. However the undiluted Resbond 791 paints were applied using a brush, since it is difficult to spray and does not give the desired uniform coating.

Table 2. TSP sample matrix for three binders.

Resbond Binder		Phosphor		Water	MgO_2
Product	**Quantity**	**Compound**	**Quantity**	**Quantity**	**Quantity**
791	35%	Y_2O_3:Eu	20%	35%	10%
	40%			40%	0%
	70%			0%	10%
	80%			0%	0%
792	70%	Y_2O_3:Eu	20%	0%	10%
	80%			0%	0%
793	80%	Y_2O_3:Eu	10%	0%	10%
			20%	0%	0%

Experimental Method

In order to determine the survivability for a TSP, samples were thermally cycled in a Thermoline 46200 high-temperature furnace. The furnace controls were set to raise the temperature to some predetermined value. The sample was then allowed to remain at this high temperature for one hour or more, followed by cooling to ambient room conditions. To quantify the fluorescence efficiency of phosphor suspended in the TSP, a Perkin Elmer LS-50B spectrophotometer was used to measure the emission spectrum of the sample after each thermal cycle. For each TSP mixture, two samples were made. The first sample was heated through the curing cycle and used as a control. The second was thermally cycled by heating to a set temperature and allowing it to cool back to room temperature. After the sample cooled, the emission spectrum was measured. Figure 1 shows the variation in the emission spectrum for a Resbond 793 and Y_2O_3:Eu-based TSP after thermal cycling at several different temperatures. It is quite obvious that fluorescence intensity for the 611 nm emission line decreases as a function of temperature. In fact, the 611 nm fluorescence emission is reduced to the background level after thermal cycling at 1600 °C. The TSP fluorescence spectrum shown in Figure 1 contained 80% Resbond 793 and 20% Y_2O_3:Eu by volume.

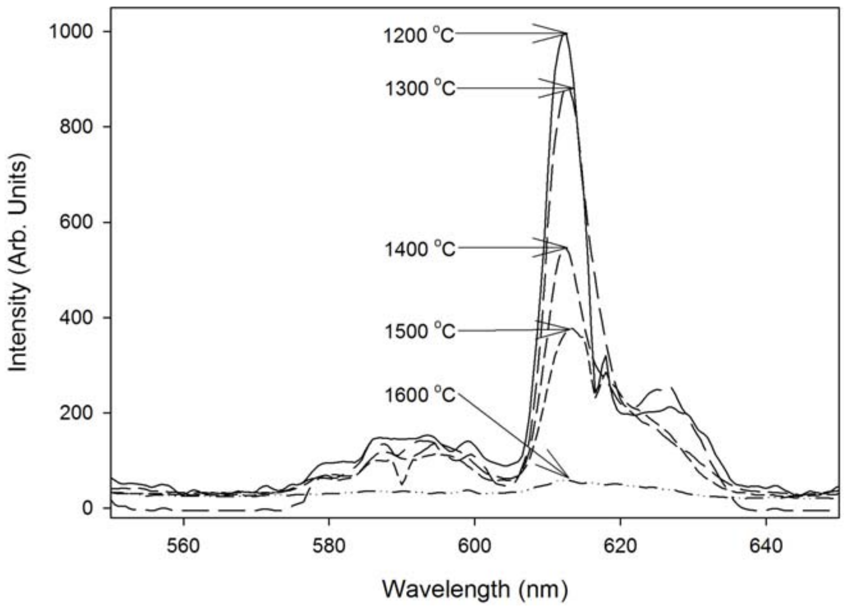

Figure 1. Resbond 793 and Y_2O_3:Eu TSP emission spectrum after thermal cycling.

Qualitative Results

After thermal cycling, TSP samples were analyzed under a ultraviolet light to qualitatively estimate the intensity of the remaining 611 nm fluorescence from Y_2O_3:Eu. The TSPs were held at temperature for one hour. Qualitative results for the MgO_2-based Resbond TSP samples are shown in Table 3. Notice that all of the tested TSP samples showed some fluorescence after thermal cycling to 1300 °C. Fluorescence was also observed for all but one TSP sample at 1400 °C. Only one MgO_2-based TSP made with Resbond 792 showed significant fluorescence at 1500 °C. None of the MgO_2-based TSPs survived to 1600 °C. These results are consistent with earlier TSP research completed during the NASA-Glenn program [ref. 7-12].

Table 3. Qualitative results for the MgO_2-based TSP samples.

Resbond Binder		**Remaining Paint Components**			**Phosphor Emission At Given Cycling Temperature?**				
Type	**Amount**	**Y_2O_3:Eu**	**Water**	**MgO_2**	**1200 °C**	**1300 °C**	**1400 °C**	**1500 °C**	**1600 °C**
791	35%	20%	35%	10%	Yes	Yes	Yes	No	No
	70%		0%	10%	Yes	Yes	Yes	No	No
792	70%	20%	0%	10%	Yes	Yes	Yes	Yes	No
793	70%	20%	0%	10%	Yes	Yes	No	No	No

Quantitative Results

A quantitative determination of fluorescence intensity as a function of cycling temperature is more complex. It was decided to use a ratio of 0.2 (20%) of the maximum emission intensity as the criteria to determine the viability of fluorescence for a given TSP sample. If the fluorescence emission is small, it will be difficult to measure the decay time and obtain a corresponding surface temperature. There will come a point in intensity where a phosphor system cannot be used to measure temperature. The decision ratio of 0.2 was completely arbitrary and was based on the observation that the apparent fluorescence measurement uncertainty was about ± 10% (intensity fraction of 0.1), which was two times the measured error for the 611 nm line for Y_2O_3:Eu.

For each tested TSP, the spectral fluorescence intensity was measured using a Perkin Elmer LS-50B spectrophotometer with ultraviolet excitation. In each case, the fluorescence was normalized to the Y_2O_3:Eu maximum emission line at 611 nm. Samples were held at temperature for one hour. Figure 2 shows plots of peak intensity versus temperature for Resbond TSPs, made with and without MgO_2. Quantitative results for each Resbond binder can be found in the sections that follow.

The evaluation of Resbond 791 was complicated by its viscosity. The viscosity required changing the airbrush application by either increased supply air pressure or thinning of the binder. Since the other evaluated binders had smaller viscosities, it was felt that thinning of the binder would provide a more equitable comparison. As such, the binder was thinned by a one-to-one ratio with water, which aided in the application of the coating. Figure 2A shows the brushed Resbond 791 TSPs survived thermal cycling to 1400 °C. The addition of MgO_2 initially improved survivability of the coating; however past 1300 °C, the intensity decreases faster than samples tested without the added MgO_2. In order to determine the effect of thinning the binder, a second series of tests were performed using brushed-on coatings. These coatings were thicker than the airbrushed paints. Figure 2B shows that the sprayed Resbond 791 had a lower maximum survivability temperature of 1400 °C. For this configuration, the addition of MgO_2 increased the degradation of the coating. It is interesting to note that the intensity of the undiluted paint samples decreases faster than the diluted samples, which could be caused in part by differences in application technique. The undiluted samples were brushed on the surface, which was not uniform. A variable coating thickness could cause uneven heating and enhance flaking of the TSP.

Figure 2C shows the sprayed on Cotronics Resbond 792 falls below the 20% light emission criteria after 1400 °C. The addition of MgO_2 appears to slightly improve the response of the coating after thermal cycling. Unfortunately, even with this addition, the response is relatively flat at a level of approximately 25% of the peak amplitude. This test confirms that the Resbond 792 and MgO_2-based TSP was not suitable for high-temperature thermometry.

Of the three tested binders, Cotronics Resbond 793 appears to have the best qualities in its unmodified state. Figure 2D shows the survivability temperature for the Resbond 793 drops to 1300 °C with a dramatic decrease in intensity when MgO_2 is added. The Resbond 793 TSP meets the quantitative survivability criteria to 1300 °C**.** Review of the post thermal cycling data indicates that the coating remains bright and structurally intact up to 1300 °C. By 1400 °C, fluorescence emission is gone. The addition of MgO_2 does not appear to significantly affect the survivability of the Resbond 793 TSP.

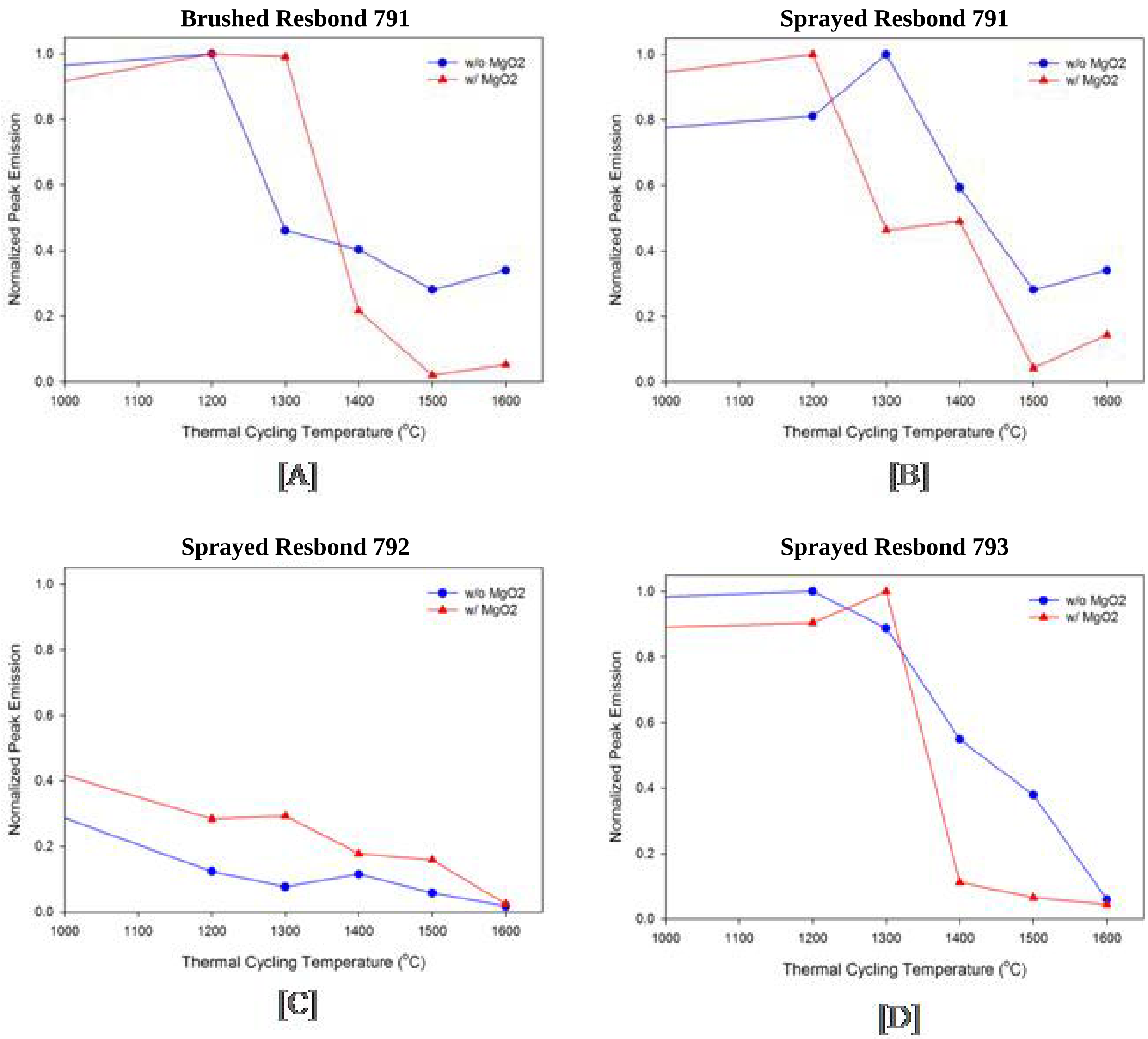

Figure 2. Effect of adding MgO_2 on the survivability of the high-temperature Resbond TSPs.

Conclusions

Phosphors are fine powders that are doped with trace elements that give off visible light when suitably excited. Some phosphors can survive and function at high temperatures such as those present during combustion. This research determined the effect of adding MgO_2 to selected Resbond-based TSPs. Notice that all of the tested MgO_2-based TSP samples showed some fluorescence after thermal cycling to 1300 °C. Fluorescence was also observed for all but one TSP sample at 1400 °C. Only one MgO_2-based TSP made with Resbond 792 showed significant fluorescence at 1500 °C. None of the MgO_2-based TSPs survived to 1600 °C. These results are consistent with earlier TSP research completed during the NASA-Glenn program. Over all samples, the addition of MgO_2 does not appear to significantly improve the thermal cycling survivability. Additional research will be completed to further quantify these results.

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