VOL. 7, NO. 10, OCTOBER 2012 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

OPTIMIZATION OF SURFACE EMISSIVITY OF SOL-GEL NANO-COMPOSITE COATINGS FOR THERMAL DISSIPATION WITH TAGUCHI DESIGN OF EXPERIMENTS

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ABSTRACT

Coatings composed of hybrid ceramic nano-particles in different sol matrices were prepared by sol-gel spray coating method. Coating formulation was optimized using Taguchi design of experiments method. The variables selected were the type of sols and the content of SiC, zinc oxide and Al_2O_3. An orthogonal array of L9 (34) was used; Signal-to-noise (S/N) ratio and Analysis of Variance (ANOVA) were used to identify the significant factors affecting infra red emissivity and physical properties to give optimum coating formulation. The thermal infrared emissivity of the coatings was determined using IR-1 emissiometer. The pencil hardness and adhesion tests were conducted to evaluate the coatings for potential industrial applications. The coating solutions were applied onto sand blasted aluminum substrates. High emissivity values ranging from 0.917-0.941 were obtained. Results indicated that hybrid nano-particles can be dispersed in sol to give coatings with good thermal emission properties and are a potential candidate for passive cooling applications. The coatings can be prepared in an easy controlled way using sol-gel method and show good physical properties.

Keywords: ceramic nano-particles, sol gel, infrared emissivity, design of experiments, Taguchi.

INTRODUCTION

High emissivity coatings

High emissivity coatings have received a lot of attention in the recent past especially for space applications [1, 2] and radiative cooling applications [3, 4]. There has been great advancement in the field of electronics leading to increase in processing power and miniaturization of electronic components. This has led to generation of large amounts of heat which needs to be dissipated away fast to avoid damage to the electronic parts or degradation of performance. High emissivity coatings can dissipate heat fast using radiative thermal transfer, which can be determined by the thermal infrared emissivity in the wavelength range of 8-14 µm. Emissivity is measured by comparing the emission from a sample to an ideal black body, which emits radiation at an emissivity of 1. Thermally emitted radiation from any surface mainly depends on the surface temperature and the surface emissivity. Surface temperature signifies energy balance between the body and the surroundings while surface emissivity is the efficiency of the surface for dissipating the radiant energy generated in the surface into its surroundings.

These coatings have been synthesized using methods such as Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD), and Electron Beam Physical Vapor Deposition (EB-PVD) [5]. However, most of these methods require very high processing temperatures and advanced equipment which may not be readily available. The sol gel method is a versatile method for deposition of coatings and thin films due to its ease of preparation at lower temperatures [6] and the ability to control the microstructure. In the sol gel composite process, ceramic nano-particles are dispersed in sol and the sol gel derived phase acts to bind the powder phase internally. This method was first reported by Barrow and Petroff [7] and later used by T. Olding and others [8-10]. A strong and hard coating is formed because the film forms a strongly bonded network, with a sol gel film firmly bonded between ceramic particles, reducing the likelihood of crack formation in the film during processing. In addition, since the quantity of sol used is greatly reduced because of the presence of ceramic nano-particles, there is less shrinkage after processing the film [8].

The Taguchi approach

The Taguchi design of experiments method is based on an orthogonal array with a robust design which is aimed at minimizing response variation. Because of this, each factor can be evaluated independent of all the other factors, so the effect of one factor does not influence the estimation of another factor. After careful selection of factors that affect the response, settings are made that will reduce the variation indicated by changes in signal -to-noise ratios. It introduces an integrated approach that is simple and efficient to find the best range of designs for quality, performance and computational cost [11]. This method achieves the integration of design of experiments (DOE) with the parametric optimization of the process yielding the desired results. The Taguchi's method utilizes the S/N ratio also defined as the ratio of the mean (signal) to the standard deviation (noise) to perform response analysis. It uses a logarithmic function of desired output to serve as objective functions for optimization. The method offers three categories for calculation of S/N ratios: larger is best, lower is best and nominal is best [12]. For each response, the appropriate category is selected based on whether maximizing or minimizing the value is the goal.

VOL. 7, NO. 10, OCTOBER 2012 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

In the current study, the larger-is-better characteristic was used because higher emissivity values are desirable. In addition, a statistical ANOVA is performed to find which parameters are statistically significant. The combination of S/N ratios and ANOVA analysis tools allows for the prediction of optimal combination of factors giving the best responses. Finally, a confirmation experiment is conducted to verify the optimal process parameters obtained from the parameter design.

EXPERIMENTAL DETAILS

Coating preparation

Materials

For the silica based matrix, Tetraethoxysilane (TEOS) was used as the main precursor while Methyltrimethoxysilane (MTMS) was used as a modifier. Acetic acid was used as the catalyst to control the pH of the solution. For the Titania matrix, Titanium (iv) Butoxide was used as the main precursor with ethanol as the solvent. Acetyl acetone was used as the chelating agent to control the rate of reaction. A combination of SiC, aluminum oxide and zinc oxide nanoparticles (average 40 nm particle sizes) was introduced to improve thermal radiation and give a compact structure. These materials were supplied by Shanghai Excilon New Materials Technology Company and used as received.

Preparation of sols

Three different sols were prepared in this study. Silica sol was prepared by hydrolysis and condensation of TEOS in the acidic environment, and then modified using MTMS. Another sol was prepared by the hydrolysis and condensation of MTMS in the presence of colloidal silica in acidic media. Finally, titanium oxide sol was prepared by the hydrolysis of Titanium (iv) Butoxide in ethanol with acetyl acetone as a chelating agent.

Preparation and deposition of coating solutions

The prepared sol solutions were measured into small bottles and then nanoparticles were added together with other additives. The mixture was then subjected to a vibratory ball mill for one hour using ceramic balls. The mixture was then sieved and sprayed onto aluminum plates using a hand held air spraying gun. All the plates were sandblasted using Al_2O_3 particles at an air pressure of 3 bars and washed with dilute sodium hydroxide solution. The plates were then rinsed with water and dried in an oven. The deposited coatings were then dried in an oven at 80°C for 30 minutes and cured at 260°C for one hour. The effect of filler content of different nanoparticles and the type of sol precursor were investigated using the Taguchi design of experiments L9 orthogonal array.

DESIGN OF EXPERIMENTS

An orthogonal array is employed based on the Taguchi orthogonal method, which reduces the number of experiments for determining the optimal coating process parameters. With an orthogonal array, it is possible to vary all the parameters to consider their direct effect as well as interactions simultaneously using the shortest possible matrix combinations. This way, the number of runs can be reduced effectively hence saving on time and costs [13]. The current study comprises an L9 orthogonal array with 9 rows corresponding to the number of runs (8 degrees of freedom) and 3 columns corresponding to the design response. The factors varied were type of sol precursor, content of emissivity agent SiC, content of zinc oxide and content of alumina. The resulting responses evaluated were infra-red emissivity, pencil hardness and coating adhesion. Table-1 shows the orthogonal array with design factors and the assigned codes and Table-2 shows the factors and the assigned levels.

Table-1. Orthogonal array with coded values.

Run	Control factors and levels			
	A	**B**	**C**	**D**
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table-2. Factors with assigned levels.

Factors		Low (1)	Mid (2)	High (3)
A	Type of sol	TEOS sol	MTMS sol	TiO_2 sol
B	Al_2O_3 (wt %)	10	12.5	15
C	SiC (wt %)	2.5	3.75	5
D	ZnO (wt %)	5	7.5	10

ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

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Characterization and testing

The surface morphology was studied using the Scanning Electron Microscope (SEM). The thermal infrared emissivity was determined using an IR-1 emissiometer at the Shanghai institute of technical physics at wavelengths of 8-14 µm at ambient temperature.

Physical properties were also tested for possible industrial application. The pencil hardness test was conducted according to the ASTM D3363-05 standard using pencils in the range 6B-9H, in ascending order of hardness. The pencils lines were drawn manually using the hand. If a scratch was made on the surface, the lower pencil number was taken as the hardness.

Coating adhesion was performed according to the ASTM D 3359 standard based on the cross cut/tape method. In this method, 1 mm cross hatch scratches was made on the coating surface with a sharp blade to form small squares. A tape was then adhered to the surface on the squares and pulled back strongly. The surface was then visually inspected for crack formation or removal of coating and graded on a scale as provided in the test standard.

RESULTS AND DISCUSSIONS

The Taguchi design was analyzed using the Statistica Design and Analysis software. The S/N ratio for larger-the-better characteristic was chosen for infra-red thermal emissivity, adhesion and pencil hardness. This is because high values are desired for these responses. The generic form of S/N ratio then becomes:

$$S/N = -10*\log10 (1/N*Sum (1/y^2))$$

The S/N ratios for all the responses are given in Table-3. The mean of these S/N ratios at each level of process variable or affecting factor is summarized in Table-4 and Figure-1. The ranks obtained for each factor determines its effect on the thermal emissivity, adhesion and hardness of the coatings.

Table-4 shows that the content of Al_2O_3 plays a major role in increasing the emissivity of the coating since there was an increase in the emissivity value with increase in its content. This could be attributed to thermal radiation through photon transfer caused by electron transport. This was confirmed by L. Brginsky *et al*., when they found that an Al_2O_3 crystal shows no resistance to photon transport and contributes considerably to the radiative component of thermal transfer due electron levels localized at less than 0.1 eV from a band edge [12].

The findings also indicate that the kind of sol also has a strong effect on infrared emissivity, with Figure-1 (a) showing that the sol from MTMS hydrolysis gives the highest emissivity. This is in line with the findings of C. A. Sizemore *et al.*, when they studied release of radiative energy from organofunctional silanes due to molecular vibration. Higher emissivity is obtained from materials with lighter functional groups due to higher vibrational frequencies [14].

Table-3. Response table for signal to noise ratios.

Run	Emissivity (%)	S/N Ratio (dB)	Adhesion	S/N Ratio (dB)	Hardness	S/N Ratio (dB)
1	91.7	39.24739	4B	12.04120	6B	15.56303
2	93.9	39.45331	5B	13.97940	6B	15.56303
3	92.0	39.27576	4B	12.04120	6B	15.56303
4	92.5	39.32283	3B	9.54242	8B	18.06180
5	93.9	39.45331	3B	9.54242	8B	18.06180
6	94.1	39.47179	3B	9.54242	8B	18.06180
7	91.5	39.22842	5B	13.97940	3B	9.54242
8	93.2	39.38832	5B	13.97940	2B	6.02060
9	93.7	39.43479	5B	13.97940	2B	6.02060

VOL. 7, NO. 10, OCTOBER 2012 ISSN 1819-6608
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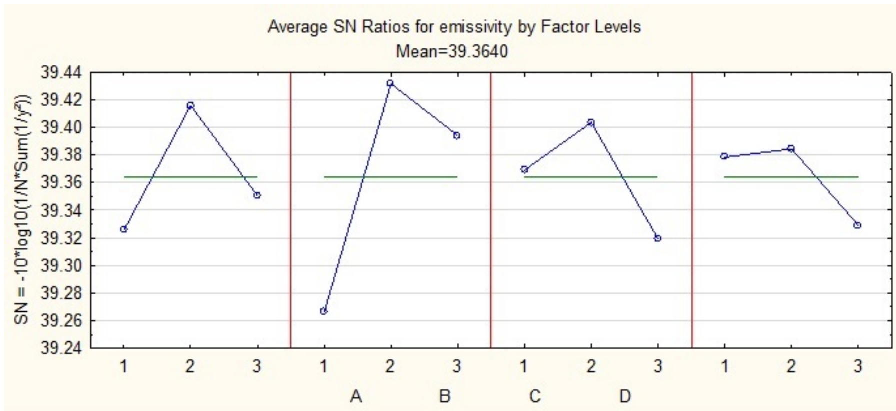
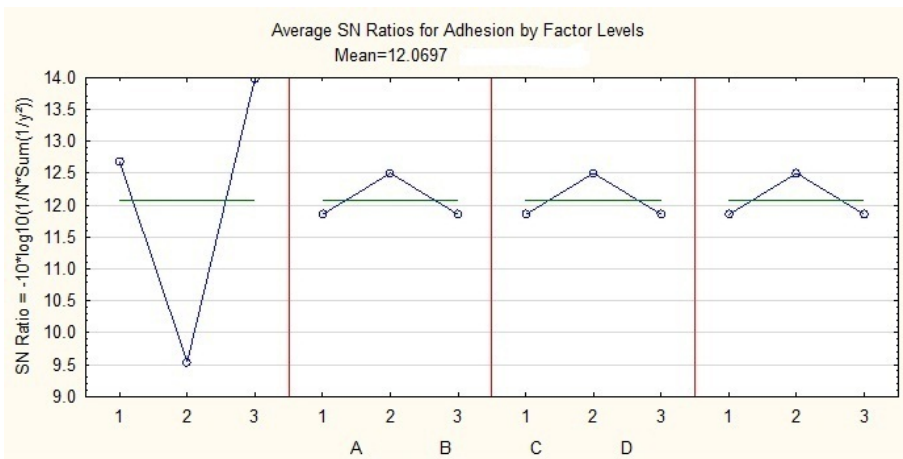


(a)



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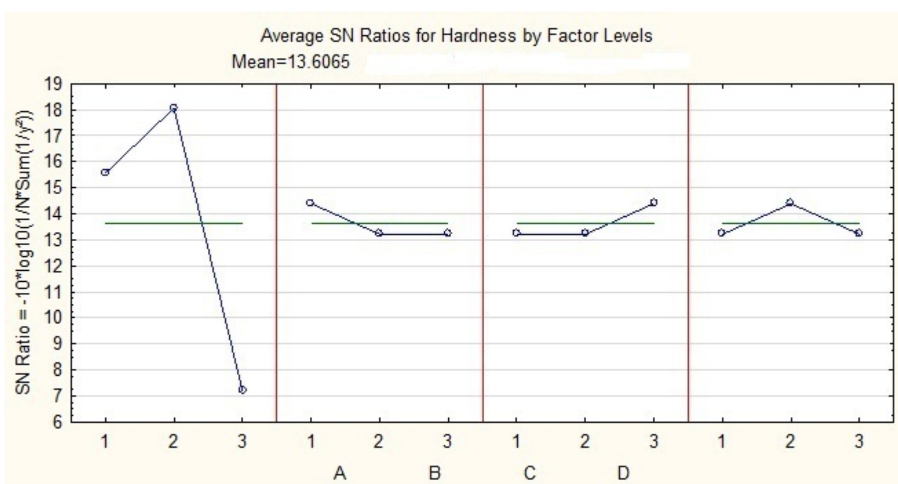

(c)

Figure-1. Average S/N ratios by factor levels for (a) Emissivity (b) Adhesion and (c) Hardness.

Although SiC is a high emissivity material, it comes third in S/N ratio ranking and f-value in Table-4. Its influence has been surpassed by factors A and B, probably due to the microstructure brought about by factors A and B. The content of ZnO was found to have the least effect on emissivity.

The results also indicate that only the kind of sol matrix has a significant influence on both the coating hardness and adhesion as s in Table-4 and Figures 1(b), (c) with all the other factors except A (type of sol) displaying equal delta and signal noise ratios. This could be attributed to the state of the nano-structured coating whereby the nanoparticles are finely distributed within the coating structure.

Table-4 shows that coatings with TiO_2 sol have the best adhesion but have poor hardness, while the ones with MTMS sol shows the best hardness and poor adhesion. The TiO_2 coating has porous structure with rougher surface (Figure-2) which contributes to the adhesion by providing larger contact area and anchoring effect between the coating and the substrate, but reduces the hardness. The coating with MTMS is more compact resulting in good pencil hardness (Figure-3).

Table-4. Mean of S/N ratios at individual levels.

Level	Emissivity				Adhesion				Hardness			
	A	**B**	**C**	**D**	**A**	**B**	**C**	**D**	**A**	**B**	**C**	**D**
1	39.33	39.27	39.37	39.38	12.69	11.85	11.85	11.85	15.56	14.39	13.22	13.22
2	39.42	39.43	39.40	39.38	9.54	12.50	12.50	12.50	18.06	13.22	13.22	14.39
3	39.35	39.39	39.32	39.33	13.98	11.85	11.85	11.85	7.20	13.22	14.39	13.22
Delta	0.09	0.16	0.08	0.05	4.44	0.65	0.65	0.65	10.86	1.17	1.17	1.17
Rank	2	1	3	4	1	2	2	2	1	2	2	2

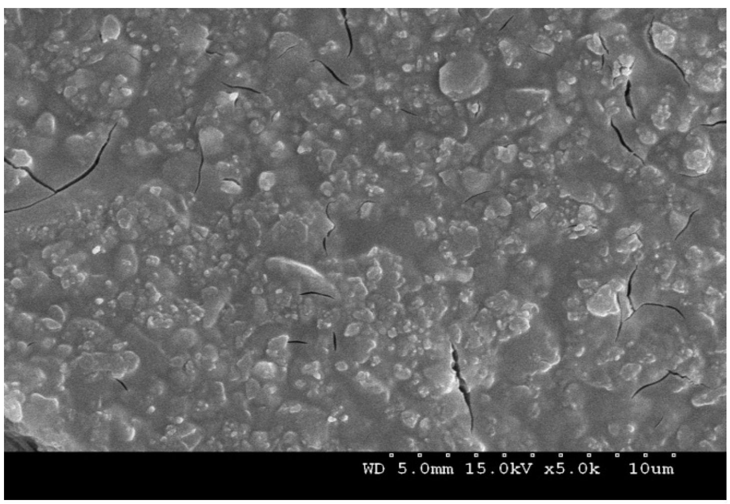

Figure-2. SEM pictogram of TiO_2 sol based coating.

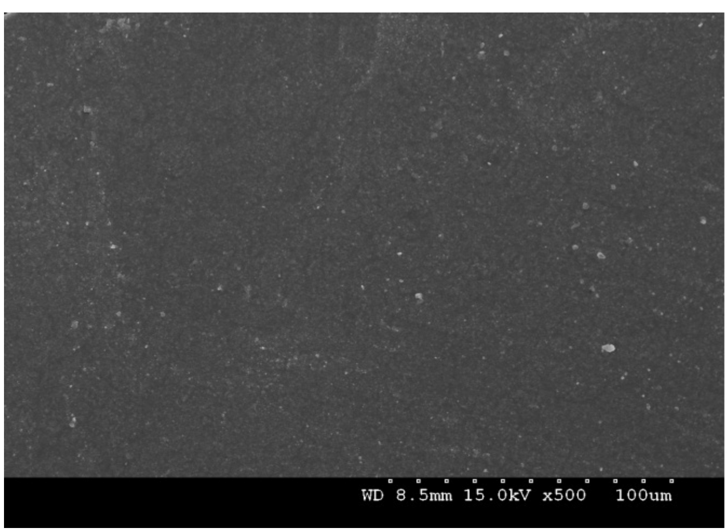

Figure-3. SEM pictogram of MTMS sol based coating.

The ANOVA analysis was also used to investigate the effect of various factors on the response. Because the current L9 design has nine runs with 8 degrees of freedom, there is no degree of freedom left for the error factor in the ANOVA analysis. Therefore, the factor with the least mean of squares was pooled into the error factor to provide two degrees of freedom as shown in Table-5. The ANOVA analysis indicates that factor B has the highest f-ratio, which indicates statistical significance of the factor. Factor A was next significant, with sol from MTMS precursor showing the highest effect followed by TiO_2 sol. Sol from TEOS hydrolysis showed lowest effect on the response. The next significant factor was factor C, with medium loading showing increased effect.

Table-5. Analysis of variance for emissivity.

Effect	SS	Df	MS	F	p
A	0.013102	2	0.006551	2.350665	0.298448
B	0.045135	2	0.022568	8.097950	0.109915
C	0.010826	2	0.005413	1.942440	0.339854
D*	0.005574	2			
Residual	0.005574	2	0.002787		

SS sum of squares, Df degree of freedom, MS Mean of squares, F f-ratio, p contributing ratio
* - effect pooled into error term

High level of factor C reduces the S/N ratio implying that emissivity increases as the content of SiC increases but it reaches an optimum level where further addition does not in increase the emissivity further [15]. Factor D was least significant and was pooled into the error term as described before. From the SN ratios (Table-4), it was clear that only one factor was significant for the adhesion and physical test and therefore analysis of variance was not conducted.

Selection of the optimum levels of the design factors produces an optimum coating for this particular application. Table-5 shows the optimum conductions for producing the best coating under this study. The coating would have high thermal infrared emissivity, high adhesion and good pencil hardness for industrial application.

Table-5. Expected S/N ratios under optimum conditions.

Factor	Level	Effect
A	2	0.05199
B	2	0.06766
C	2	0.03965
D	2	0.02052
Expected S/N ratio (dB)		39.54

To validate the proposed experimental methodology, coatings were prepared using the optimum levels of each individual factor. The experimental data showed an enhanced S/N ratio of 39.52, which is very close to the predicted value (39.54) that was obtained from the statistical evaluation.

CONCLUSIONS

The Taguchi orthogonal array design of experiments method has been used to optimize the coating process parameters with respect to thermal emission behavior of sol-gel nano-composite coatings on aluminum substrates.

Sol-gel solutions were prepared successfully using different precursors and coating solutions prepared by dispersing ceramic nanoparticles. It was found that the content of Al_2O_3 and the kind of sol used have the most significant influence in controlling thermal radiation characteristics of sol-gel hybrid coating. The optimal coating parameter combination for maximum thermal emissivity is obtained as $A_2B_2C_2D_2$.

The coatings display good physical properties and have a high potential in radiative cooling applications. More research will be carried out to determine the actual cooling efficiency of the coatings.

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