A Statistical Prediction of Multiple Responses Using Overlaid Contour Plot on Hydroxyapatite Coated Magnesium via Cold Spray Deposition

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Abstract

This work aimed to search optimal values for the properties of hydroxyapatite coated pure magnesium produced by cold spray deposition. Using fractional factorial design ($2^{k-1}$), standoff distance, surface roughness and substrate heating temperature during cold spraying were selected as significant factors while number of sprays as insignificant factor. The responses chosen are coating thickness, hardness and elastic modulus of the coating. The analysis of the contour plots for thickness revealed that high thickness (>40µm) was obtained when standoff distance is at 20-25mm, surface roughness at 240-700 grit and substrate heating temperature at 350-550°C. High nanohardness (>400 MPa) obtained when standoff distance is at 20-35mm, surface roughness at 240-900 grit and substrate heating temperature at 350-550°C. High elastic modulus (>40GPa) was obtained at 20-30mm for standoff distance, 240-800 grit for surface roughness and 350-550°C for substrate heating temperature. The contour plot of coating thickness, nanohardness and elastic modulus were overlaid to find the feasible region.

Keywords: multiple responses; overlaid method; cold spray

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1. Introduction

Biomaterials are defined as any synthetic material that is used to replace or restore function to a body tissue and is continuously or intermittently in contact with body fluids. The ideal biomaterials must meet a variety of different criteria, depending upon the application. The majority of orthopedic replacements are used in load-bearing situations such as total hip replacements or dental applications, resulting in the need for biomaterials with strong mechanical properties. In addition to providing mechanical strength the biomaterial must also be non-toxic to cells and living tissues. Metal implants provide the most suitable mechanical properties for these applications, as polymeric and ceramic materials tend to be relatively weak or brittle. Titanium and titanium alloys, stainless steels, and cobalt-chromium alloys are all used in joint replacement procedures and generally provide suitable mechanical support to restore orthopedic function. In comparison with titanium alloys and stainless steel, biodegradable magnesium alloys are identified as revolutionizing biomaterials. Magnesium (Mg) alloys have been suggested for biomedical application due to their potentials to serve as biodegradable metallic implants since they can be gradually dissolved, consumed or excreted in human body and then disappear after bone tissues heal. Magnesium ions present in the human body, whereby approximately 1 mol of Mg is sorted in a 70 kg adult human body and an estimated amount of half of total physical Mg in the bone tissue. Elastic modulus of pure Mg is about 40-45 GPa which is very close to that human bone (10-40 GPa) so it can reduce the chance of stress shielding effects observed in the case of higher modulus materials such as titanium. In this study, pure Mg has been used as Mg alloys is generally not advisable because most alloying elements can be toxic to the human body.

The ability of metal implants to be incorporated into the natural bone structure, however, has posed problems and caused significant load-bearing differences that often result in implant failure. To counteract this problem, various coatings have been applied to metal implants to promote bone growth and improve the implant-to-bone transition. A number of calcium phosphates have been shown to produce no adverse biological reactions when implanted within the body. Furthermore, studies have characterized certain calcium phosphates, most notably hydroxyapatite (Ca_{10}(PO_{4})_{6}(OH)_{2}), shown that bone adheres well to, and forms a bond with, these surfaces. By coating metallic implants with calcium phosphates, it is possible to combine the mechanical strength of the metal with the biological compact of the mineral. Calcium phosphate coatings have been shown to be successful in promoting bone apposition and growth in vivo, and clinical studies have confirmed the efficacy of orthopedic implants coated with hydroxyapatite. This success has spurred a significant amount of research aimed at understanding and optimizing the properties and behavior of these coatings. Conventionally, bioceramic such as HAP have been deposited by plasma spray technique. However, due to the inherent high temperature in plasma spray, the deleterious effect such as phase alteration, evaporation and debonding occur by this coating technique. In this regard, colds spray can be a good alternative for coating deposition at temperature well below the melting point. Cold spray is a process in which solid powders are accelerated in a de Laval nozzle toward a substrate. Cold spray has emerged as a promising process to deposit nanostructured materials without significantly altering their microstructure whereas many traditional consolidation processes do. In conventional cold spray technique hot gases at temperatures 500-700°C is used as carriers of the sprayed powders while the substrate remains at room temperature. In the present study, the cold spray technique was modified by using ambient air at room temperature as the spraying medium and heating the substrate to 400°C. This modification helped in retaining the HAP properties which usually show phase changes at high temperature deposition.

Design of experiment (DOE) is one widely used experimental study methods on many processes in engineering. It is a statistical approach in which a mathematical model is developed through experimental runs. Besides, it provides the researchers or users the opportunity to optimize and predict possible output based on the parameter setting. In practice, the DOE method has been used successfully in several industrial applications for optimizing manufacturing processes. For example, DOE has been applied to optimize the plasma spray process of yttria-stabilized zirconia coatings. Of the available DOE methods, a fractional factorial design is a variation of the basic factorial design in which only a subset of the run is used. These fractional factorial designs are among the most widely used types of
designs for product and process designs and for process improvements. In developing the regression equation, the test variables were coded-according to the following equation:

\[ X_j = \frac{(Z_j - Z_{0j})}{\Delta_j} \]  

(Eq.1)

Where \( X_j \) is the coded value of the independent variable, \( Z_j \) is the real value of the independent variable; \( Z_{0j} \) is the value of the independent variable on the center point, and \( \Delta_j \) is the step change value. On the other hand, multiple response optimization methodology is a collection of mathematical and statistical techniques for designing experiments, building models, evaluating the effects caused by factors, and searching for optimum conditions for the modeling and analysis of multiple response optimization problems. The multiple responses of interest are influenced by several variables. The aim is to optimize these responses. Frequently, the overlaid method analysis is employed to determine the tradeoff optimal values from multiple regressive equations. In this work, a novel approach by adopting the cold spray technique to coat HAP on a magnesium substrate at low temperature is proposed. As far as the authors are concerned, most of published reports are limited to the effects of the process parameters on a single response.

2. Materials and Methods

2.1. Sample preparation

Pure Mg plate provided by Xi’an Yuechen Metal Products, China was cut into 15 mm x 15 mm x 5 mm. Before the cold spray process, the samples were pre-treated as follows: (1) the specimen surfaces were serially ground with either 240 grit or 2000 grit SiC papers and (2) the specimens were cleaned ultrasonically in acetone for 5 min. For HAP, Ca10(PO4)6OH2 powder (Sigma-Aldrich, Malaysia) was used as the feedstock for the cold spray process. The pure Mg substrate was placed inside a furnace, where it was preheated to a temperature of either 350°C or 550°C for 1 hour, and then the HAP powder was cold-sprayed onto the substrate. The nozzle was positioned at either 20 mm or 40 mm from the preheated substrate with the spray angle between the nozzle and substrate maintained at 90°. The air pressure was 1MPa and the air temperature was maintained at room temperature. The procedure was repeated either five or ten times.

2.2 Multi Regression Equation Modeling using Fractional Factorial Design

<table>
<thead>
<tr>
<th>Variable</th>
<th>Notation</th>
<th>Unit</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standoff Distance</td>
<td>X₁</td>
<td>mm</td>
<td>20</td>
</tr>
<tr>
<td>Surface Roughness</td>
<td>X₂</td>
<td>grid</td>
<td>240</td>
</tr>
<tr>
<td>Substrate Heating Temperature</td>
<td>X₃</td>
<td>°C</td>
<td>350</td>
</tr>
<tr>
<td>Number of sprays</td>
<td>X₄</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

A 2⁴⁻¹ fractional factorial design with two replications was used to pick factors that influenced the mechanical properties of the coating sample significantly and any insignificant ones were eliminated to obtain a smaller and more manageable set of factors. This DOE design was carried out using Minitab 16 (Minitab Inc. USA). To avoid too wide range in the screening tests, the range of factors used was designated as +1(high) or −1(low), as given in Table 1. The
levels of the factors were chosen based on preliminary experiments. Analysis of variance (ANOVA) was used to determine the adequacy of the factorial model. Then, optimization experiments were performed to determine the best settings and define the nature of curvature of the response curves.

2.3 Characterizations of HAP coatings

Coating thickness was measured using a field emission scanning electron microscope (FESEM-Zeiss Supra 35VP-24-58). Hardness and the elastic modulus of the coating were evaluated by nanoindentation with a nano test instrument (Micro Materials Ltd, Wrexham, UK) at minimum and maximum loads of 10 mN and 300 mN. The indentations were made under load control mode, where the loads were applied and then released after the set peak with dwell times of 5 s at the maximum loads.

3. Results and Discussion

3.1 Fractional Factorial Design

Optimization of parameters like standoff distance (X1), surface roughness (X2), substrate heating temperature (X3), and number of sprays (X4) were investigated. In this study, the influence of various process parameters on HAP coated onto pure Mg substrate were investigated via a screening process using fractional factorial design.

Table 2: Effects and regression coefficients for thickness, nanohardness and elastic modulus of coatings

<table>
<thead>
<tr>
<th>Variable</th>
<th>Thickness</th>
<th>Nanohardness</th>
<th>Elastic Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Regression Coefficient</td>
<td>Estimated Effect</td>
<td>p-value</td>
</tr>
<tr>
<td>Constant</td>
<td>26.3843</td>
<td>29.774</td>
<td>0.000</td>
</tr>
<tr>
<td>X_1</td>
<td>-5.8720</td>
<td>-6.626</td>
<td>0.000</td>
</tr>
<tr>
<td>X_2</td>
<td>-5.2025</td>
<td>-5.871</td>
<td>0.000</td>
</tr>
<tr>
<td>X_3</td>
<td>3.4730</td>
<td>3.919</td>
<td>0.04</td>
</tr>
<tr>
<td>X_4</td>
<td>0.0365</td>
<td>0.041</td>
<td>0.968</td>
</tr>
<tr>
<td>X_1 X_2</td>
<td>3.2702</td>
<td>3.690</td>
<td>0.006</td>
</tr>
<tr>
<td>X_1 X_3</td>
<td>-1.0368</td>
<td>-1.170</td>
<td>0.276</td>
</tr>
<tr>
<td>X_1 X_4</td>
<td>0.8493</td>
<td>0.958</td>
<td>0.366</td>
</tr>
</tbody>
</table>

The factorial analysis of variance in Table 2 indicates that the standoff distance, surface roughness, and substrate heating temperature were significant factors (p value of < 0.05 was used as a cutoff point for significance differences), which affects the mechanical properties of the coating sample and number of spray factor were found to be insignificant parameters and were maintained as a constant. A linear regression equation could be obtained from the regression results of the fractional factorial experiment:

\[ Y_1 = 29.1 - 0.294X_1 - 0.591X_2 + 0.347X_3 \]
\[ Y_2 = 207 - 4.21X_1 - 1.8835X_2 + 0.47X_3 \]
\[ Y_3 = 27.4 - 0.401X_1 - 0.644X_2 + 0.424X_3 \]
Based on Eq(s). 3, 4, and 5, the standoff distance, surface roughness, and substrate heating temperatures have different effects on the responses. Standoff distances and surface roughness are negative while the substrate heating temperature is positive. This shows that the factors with positive coefficients have to be increased and those with negative coefficients have to be lowered for maximizing the responses.

3.2 Overlaid Analysis for Multiple Regression

Response contour plots were generated from the model equations (Eq(s). 3, 4, and 5) obtained in the regression analysis. Fig. 1 shows the analysis of the contour plots for thickness, which revealed that high thickness (> 40 μm) was obtained at any one of the following combinations: (a) standoff distance 20–25mm, surface roughness < 500 grit, substrate heating temperature 350°C; (b) standoff distance 20–30mm, substrate heating temperature 440–550°C, surface roughness 240 grit; and (c) surface roughness 350–700 grit, substrate heating temperature 440–550°C, standoff distance 20 mm.

The analysis of the contour plots for nanohardness revealed that high nanohardness (> 400MPa) was obtained at any one of the following combinations: (a) standoff distance 20–35 mm, surface roughness 20–900 grit, substrate heating temperature 350°C; (b) standoff distance 20–30mm, substrate heating temperature 490–550°C, surface roughness 240 grit; and (c) surface roughness 350–600 grit, substrate heating temperature 490–550°C, standoff distance 20 mm. Meanwhile, for elastic modulus revealed that high elastic modulus (> 40MPa) was obtained at any one of the following combinations: (a) standoff distance 20–30 mm, surface roughness 20–600 grit, substrate heating temperature 350°C; (b) standoff distance 20–30mm, substrate heating temperature 450–550°C, surface roughness 240 grit; and (c) surface roughness 350–800 grit, substrate heating temperature 460–550°C, standoff distance.

The coating thickness, nanohardness, and elastic modulus were overlaid using Eq(s). 3, 4, and 5 and the contour plot to find the feasible region (shown as the white region) having the desired properties (Fig. 2). For overlaying, substrate heating temperature and surface roughness were chosen as variables keeping the values of standoff distance.
constant at low point (Fig. 2(a)). The desired values of all these properties could be obtained at any given combination within the optimized region. Two more feasible regions were obtained (Fig. 2(b), 2(c)).

Fig. 2. Overlaid contour plot for thickness, nanohardness and elastic modulus

3.3 Multiple responses Optimization

Multiple response optimizations are a method of analysis to identify the combination of input variable settings that jointly optimize a set of responses. Within Minitab 16 software, the response optimizer function provides an optimal solution for the input variable combinations and sometimes an optimization plot. The field expert rationally able to nominate or eliminate the combinations of trade-off optimal values according to the outcome potentiality since the optimizer is working as a composite desirability component. The optimal solution (optimal operating conditions) was determined by maximizing the composite desirability. In Fig. 3, all the responses were treated equally important and the default value 1.0 was given for \( d = 1 \). The Response Optimizer in Minitab suggested the potential combination of the input variable settings that jointly optimize three responses the thickness (Y1) as 46.2575 μm, nanohardness (Y2) as 436.4550 MPa and elastic modulus (Y3) as 43.890 GPa and provided the trade-off values of standoff distance as 22.7 mm, surface roughness as 649.2 grit, and substrate heating temperature as 495.27°C parameters that can relatively accommodate the optimum requirement of the cold spray process.
4. Conclusion

The effects of input factors such as standoff distance, surface roughness, substrate heating temperature, and the number of sprays on the mechanical properties (thickness, nanohardness, and elastic modulus) of the HAP coating on pure Mg have been investigated using fractional factorial design. The model terms attained for standoff distance, surface roughness, and substrate heating temperature were found to be significant for all responses. The overlaid contour plot indicates from the contour plot from these responses are critical to determine the tradeoff optimal values. The optimal solution has been determined by maximizing the composite desirability. The response optimizer indicated that 22.7mm standoff distance, 649.2 grit surface roughness and 496°C substrate heating temperature produced hydroxyapatite coating of 46.3μm thickness, 436.5MPa nanohardness and 43.9GPa elastic modulus was obtained to have maximum desired responses with desirability of 1.

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