Steel pipe-lined Fe–W$_2$B-based composite coating by centrifugal-Self-propagating high-temperature synthesis process

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In this study, Fe–W$_2$B-based composite coating on the inner surface of a steel pipe was produced by centrifugal- Self-propagating high-temperature synthesis (SHS) process. There were FeWO$_4$, B$_2$O$_3$, and Al powders as the major reactants. The effects of coupled additives X(Fe$_2$O$_3$–Al) of X = 1, 3, and 5 molar ratio on morphology, composition and micro-hardness of the obtained composite coatings were investigated. The results showed that the system of X = 1 mole was the optimum condition due to its reasonable smoothness (6.5 µm) and hardest (727.90 and 1170.71 HV on alloy and ceramic layers, respectively).

Key-words : Ceramics, Composites, Coating, Self-propagating high-temperature synthesis (SHS)

1. Introduction

It is well known that ceramic composite materials possess various outstanding properties including high hardness, high wear resistance, and high melting point. They are used in many military and industrial applications such as gun barrels, cutting tools, and coatings for the transportation of coal cinder, mineral powder, and oil-water mixture. The coated ceramic layers on the inner surfaces of pipes, however, were complicated. This is because the ceramic composite materials require a high energy and a long period of time to melt themselves prior to the coating process and hence a high production cost is needed for the traditional coating processes; high velocity oxygen fuel (HVOF), plasma spraying, and laser cladding. To overcome this, a novel alternative technique known as centrifugal-SHS process has been proposed with the advantages of an inexpensive and simple operation and a much shorter coating time.

Centrifugal-SHS process is a combination technique of self-propagating high-temperature synthesis (SHS) and centrifugal casting. The melted products from the SHS-reaction are separated by their densities before solidification and formation of the composite coating layers on the substrate. The ceramic composite coating is produced in one step that requires little amount of energy and time. On previous works of O. Odawara, synthesized the composite coatings consisted of metal and ceramic layers from the thermite reaction of 3Fe$_2$O$_3$ + 8Al → 4Al$_2$O$_3$ + 9Fe. Although the centrifugal-SHS process is easy to use and requires less production cost, the thermite reaction is too complex and difficult to control its mechanism. The produced composite coating was filled with porosity that needs to be improved.

Tungsten borides have been known for their high hardness and chemical inertness. They have been applied to the industries which require extremely high hardness, chemical inertness, and wear resistance, i.e., abrasive media, turbine blades, nozzle of a gas burner, crucibles and ingot molds for precision metallurgy, and thin film of electronic components. Hence, the Fe–WB composite coatings were fabricated on a steel pipe as according to our previous study, and found that the coatings consisted of a large number of pores which is undesired for many engineering applications. To improve the quality of composite coating, Fe–W$_2$B composite coating was selected to prepare in this study because its reaction was improved to achieve the simple phase of the W–B compound (W$_2$B). Another way to improve the quality of composite coating is reducing the pores by incorporating some additives into reactants such as nickel (Ni), aluminum (Al), silica (SiO$_2$), and calcium peroxide (CaO$_2$). On a point of view, because each additive offers its own advantage for pore minimization, the cooperation of two additives might result in a much better performance for this. The coupled additive of iron oxide–aluminum (Fe$_2$O$_3$–Al) was therefore used in order to minimize the number of pores presenting in the composite coatings. Its high adiabatic temperature ($T_a$) would enhance the heat of reaction that helps its products in liquid state would easily drive the heavy phase to the center. Then the gaseous phase would expedient to be eliminated. Moreover, its products would provide the FeO–Al$_2$O$_3$ spinel phase exhibiting a very high hardness as the earlier work of Xiao et al.

2. Experimental

2.1 Raw materials

The major reactants were wolframite mineral [Fe(Mn)WO$_4$, 94.76% purity, particle size < 70 µm, Sakorn minerals Co., Ltd., Thailand], aluminum (Al, 93% purity, particle size < 50 µm, Hi-Media), and boron oxide (B$_2$O$_3$, 99% purity, particle size < 80 µm, Sigma-Aldrich) powders. The additive reactants of iron oxide powder (Fe$_2$O$_3$, 97% purity, particle size < 80 µm, Sigma-Aldrich) was mixed with Al powder according to the stoichiometric requirement of reaction (1).

$$\text{Fe}_2\text{O}_3(s) + 2\text{Al}(s) \rightarrow 2\text{Fe}(s) + \text{Al}_2\text{O}_3(s) \quad (1)$$


2.2 Coating process

The overall reaction involved in SHS process for producing the composite coating is as follows.

\[
4\text{FeWO}_4(s) + 12.667\text{Al}(s) + 2\text{B}_2\text{O}_3(s) + X(\text{Fe}_2\text{O}_3 + 2\text{Al})_3(s) \\
\rightarrow 4\text{FeC}_3(s) + 2\text{W}_2\text{B}_4(s) + 6.333\text{Al}_2\text{O}_3(s) + X(2\text{Fe} + \text{Al}_2\text{O}_3)_3(s)
\]

(2)

In the coating process, the loading amount of coupled additive \((X)\) was 1, 3, and 5. All reactants were weighed by the stoichiometric requirement of reaction (2) before dry blending by ball milling about 3 h. The steel pipe samples were 2 mm thickness, 48 mm outer diameter, and 150 mm length. The samples were cleaned by polishing with a silicon-carbide (SiC) paper and rinsed with acetone. After that, each sample was sealed at the bottom with a wood plug, the blended powder was poured in, and the top was closed with a ring-shaped wood plug.

The samples were then put into the centrifugal-SHS machine as shown in Fig. 1. The rotational speed was set at a centrifugal acceleration of 125 G. Once that speed was reached, an oxygen-acetylene flame was used to ignite the SHS reaction. The reaction completed in 5 s and reached the inner coated pipe samples. They were cooled and further characterized.

2.3 Characterization

The composite coatings were characterized in terms of chemical constituents and microstructure by X-ray diffraction (XRD, X’ Pert MPD with Cu-Kα radiation, \(\lambda = 1.54 \AA\), Philips) and Scanning electron microscopy (SEM, Quanta 400, FEI) with energy dispersive X-ray spectroscopy (EDX, ISIS 300, Oxford), respectively. The surface roughness was estimated by measuring the smoothness of five sample areas per a composite coating (R\(_{a}\), SJ-210, Mitutoyo). Vickers micro-hardness was measured under a 9.81 N load held for 10 s and estimated by measuring the hardness of five sample areas per a composite coating layer (HV, HWDM-3, High Wood).

3. Results and discussion

3.1 Thermodynamic analysis

The adiabatic temperature \(T_{ad}\) of SHS reaction was calculated from the enthalphy of reaction. The maximum theoretical temperature, that the reactants can reach determining from the Eq. (3), accounts for the phase changes between the initial temperature and \(T_{ad}\).

\[
\Delta H = \int_{T_n}^{T_{ad}} C_{p,\text{solid}}dT + \Delta H_T + \int_{T_{ad}}^{298} C_{p,\text{liquid}}dT
\]

(3)

Where \(\Delta H\) is the enthalphy change, \(\Delta H_T\) is the enthalphy of transformation, \(C_p\) is the specific heat capacity, \(T_n\) is the melting temperature, and \(T_{ad}\) is the adiabatic equilibrium temperature.

The \(T_{ad}\) of each experimental condition was shown in Table 1.

In the previous studies, the researchers found that the reaction can lead to self-sustained combustion when \(T_{ad}\) exceeds 1800K or about 1527°C. Then all reactions in this study were feasible for using SHS process because their \(T_{ad}\) were more than limited level. In addition, their \(T_{ad}\) were increased when adding higher amount of the coupled additive. This would prolong the liquid state of the intermediate phases during the reaction.

3.2 Characterization results

Firstly, the composite coatings were successful produced on the inner surface of steel pipe. Figure 2 shows that the SEM images of composite coatings obtained from the coating samples containing a coupled additive at different loading amounts \((X = 0, 1, 3, \text{and } 5)\). All samples consisted of two different material layers: alloy and ceramic. Besides, the alloy layer was thicken when the loading level of coupled additive was higher. These results suggested that the formation of alloy was on the same way with the expected products as depicted in Eq. (2). The higher quantity of alloy helped to drive out the gaseous phase, so the number of pores and pore-size were decreased. The composite coating loading coupled additive at \(X = 1\) [Fig. 2(b)] was chosen the optimum condition because it had the good interfaces at both of area (substrate – alloy layer and alloy layer – ceramic layer) and a small number of pores.

As XRD patterns in Fig. 3, the composite coating with none coupled additive comprised alumina (\(\text{Al}_2\text{O}_3\)), tungsten boride (\(\text{W}_2\text{B}\)), iron aluminate (\(\text{Fe}_x\text{Al}_y\text{O}_z\)), tungsten (\(\text{W}\)), and aluminum iron (\(\text{AlFe}\)). When the coupled additive was added, the composite coatings were still made up of \(\text{Al}_2\text{O}_3\), \(\text{W}_2\text{B}\), \(\text{Fe}_x\text{Al}_y\text{O}_z\), \(\text{W}\), and \(\text{AlFe}\). These results clearly demonstrated that the formation of

Table 1. \(T_{ad}\) computed for each experimental condition of \(X(\text{Fe}_2\text{O}_3–\text{Al})\)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>(T_{ad}) (°C)</th>
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<tbody>
<tr>
<td>(X = 0)</td>
<td>2959.0</td>
</tr>
<tr>
<td>(X = 1)</td>
<td>2978.5</td>
</tr>
<tr>
<td>(X = 3)</td>
<td>3002.9</td>
</tr>
<tr>
<td>(X = 5)</td>
<td>3017.6</td>
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Fig. 1. The schematic diagram of centrifugal-SHS machine: (1) rotation direction; (2) wood-block; (3) center rest; (4) steel pipe; (5) gripper; (6) controlled speed motor.

Fig. 2. SEM images of composite coatings for all conditions used in this study; (a) \(X = 0\), (b) \(X = 1\), (c) \(X = 3\), and (d) \(X = 5\) with \(\text{Fe}_2\text{O}_3–\text{Al}\) additive.
coupled additive was not affected the product of composite coating.

SEM images in Fig. 4 shows that the microstructure of alloy layer consisted of main element, such as aluminum (Al), iron (Fe), and tungsten (W) and the ceramic layer was presented with oxygen (O), Al, and Fe. From the XRD pattern of composite coating in X = 1 condition, it suggested that the alloy layer was Fe–W2B-based composite which there were AlFe phase as matrix and W2B as reinforcement and the ceramic layer was a Fe–Al2O3-based composite. Furthermore, the W2B reinforcement phase in alloy layer was a circular-shape. Fe-based phases were still found in ceramic layer which there were AlFe phase as matrix and W2B as reinforcement and the ceramic layer was presented with oxygen (O), Al, and Fe. From the XRD pattern of composite coating in X = 1 condition, it suggested that the alloy layer was Fe–W2B-based composite which there were AlFe phase as matrix and W2B as reinforcement and the ceramic layer was a Fe–Al2O3-based composite. The coupled additive, Fe–Al2O3 offered reduction of roughness and elimination of pores. In this study, using Fe2O₃ for 1 mole was chosen as the best condition due to the highest micro-hardness value of the composite coating, reasonable smoothness, and appropriate pore size.

4. Conclusion

The Fe–W2B-based composite coatings were successfully fabricated on the inner surface of steel pipe by the Centrifugal-SHS process. The alloy layer was an Fe–W2B-based composite and the ceramic layer was an Fe–Al2O3-based composite. The coupled additive, Fe–Al2O3 offered reduction of roughness and elimination of pores. In this study, using Fe2O₃ for 1 mole was chosen as the best condition due to the highest micro-hardness value of the composite coating, reasonable smoothness, and appropriate pore size.

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References


<table>
<thead>
<tr>
<th>Conditions</th>
<th>$R_a$ (μm)</th>
<th>Micro-hardness (HV)</th>
</tr>
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<tbody>
<tr>
<td>X = 0</td>
<td>8.745</td>
<td>535.83, 1137.78</td>
</tr>
<tr>
<td>X = 1</td>
<td>6.534</td>
<td>727.90, 1170.71</td>
</tr>
<tr>
<td>X = 3</td>
<td>4.052</td>
<td>592.51, 1105.50</td>
</tr>
<tr>
<td>X = 5</td>
<td>9.831</td>
<td>595.10, 1095.20</td>
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*The micro-hardness of substrate (steel pipe) was about 145 HV.*