Short communication

Microstructural, mechanical properties and corrosion behavior of plasma sprayed NiCrAlY/nano-YSZ duplex coating on Mg–1.2Ca–3Zn alloy

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Abstract

In this study, microstructural evolution, mechanical properties and corrosion behavior of plasma sprayed NiCrAlY/nano-yttria stabilized zirconia (nano-YSZ) dual-layered coating on Mg–1.2Ca–3Zn alloy were investigated. NiCrAlY underlayer is composed of large amount of porosities and micro-cracks with thickness around 80–90 \(\mu\)m. However, nano-YSZ overlayer shows bimodal microstructure consisting of columnar grains and some partially molten parts of the nanostructured powders with thickness around 270–300 \(\mu\)m. The microhardness of dual-layered NiCrAlY/nano-YSZ coating is significantly higher than that of single-layered NiCrAlY. Despite that, the bonding strength of dual-layered coating is slightly higher than single-layered plasma sprayed coating. Results also showed that both single-layer NiCrAlY and dual-layer NiCrAlY/nano-YSZ coatings decreased the corrosion current density of Mg alloy from 217.1 \(\mu\)A/cm\(^2\) to 114.5 and 82.4 \(\mu\)A/cm\(^2\), respectively. © 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Magnesium alloy; Plasma spray; Yttria stabilized zirconia; Corrosion behavior

1. Introduction

Magnesium and its alloys are suitable replacement for iron and aluminum alloys for structural applications due to their excellent physical and mechanical properties such as low density (65% of aluminum and 25% of iron) and high specific strength \[1–3\]. Mg-alloys also received great attention from aerospace and automotive industries due to high weight reduction which leads to noticeable reduction in fuel consumption and CO\(_2\) emission \[3\]. However, poor corrosion resistance and high reactivity of Mg alloy limits their wide applications \[4–6\]. Apart from alloying, surface modifications such as plasma electrolytic oxidation (PEO), atmospheric plasma spraying (APS), ion implantation, Ca–P coatings and polymer coatings have been widely applied in order to reduce corrosion rate of Mg alloys \[7\]. Among them, APS is an effective and environment-friendly method that rapidly deposits its high-quality ceramic coating \[8\]. Fan et al. \[9,10\] reported that thermal barrier coating (TBC) on Mg alloy with 8YSZ and Al can decrease the corrosion rate of the alloy. However, there are very few reports on the corrosion behavior of NiCrAlY and NiCrAlY/nano-YSZ coated Mg–Ca–Zn in NaCl solution. Thus, NiCrAlY and NiCrAlY/nano-YSZ coatings have been deposited on Mg–1.2Ca–3Zn alloy by APS and tested in this paper. In addition, the relationship between microstructure and corrosion behavior of these coatings has been evaluated.

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Table 1
Air plasma spraying parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NiCrAlY</th>
<th>Nano-YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (A)</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Primary gas, Ar (l/min)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Secondary gas, H₂ (l/min)</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Powder feed rate (g/min)</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Spray distance (cm)</td>
<td>12</td>
<td>10</td>
</tr>
</tbody>
</table>

2. Experimental procedures

Mg–1.2Ca–3Zn alloy samples (15 × 15 × 6 mm) are used as substrates in this work. It should be mentioned that single nano-particles are not able to be sprayed due to their low mass and inertia. To address this issue, reconstitution of the nanoparticles into micrometer sized granules is vital [9]. Thus, in this study, the agglomerated nanostructured YSZ (ZrO₂–8 wt%Y₂O₃; Nanox Powder S4007, Inframat, USA) powder and a commercial NiCrAlY (Ni22Cr10Al1Y; AMDRY 962) powder with size in range of 44–65 µm were used to deposit the overlayer and underlayer, respectively. An atmospheric plasma spray (METCO, type 3MB) was used for plasma spraying of the NiCrAlY underlayer and nanostructured YSZ overlayer. The spraying parameters are summarized in Table 1. X-ray diffractometry (Siemens-D500) was used for identifying the phases present in the samples using Cu Kα radiation generated at 40 kV and 35 mA. Microstructural observation was performed using a scanning electron microscope (SEM; JEOL JSM-6380LA) and transmission electron microscopy (TEM; Hitachi). A three-electrode cell was used for potentiodynamic polarization tests (PARSTAT 2263) in 3.5 wt% NaCl solution according to [11]. Using a Vickers hardness tester (Shimadzu) with a load of 500 g and a holding time of 15 s, an average of five microhardness readings of the plasma sprayed coatings was obtained from the polished cross-section. The total porosity of single-layer NiCrAlY and dual-layer YSZ/NiCrAlY coatings was evaluated by image analysis from five backscattered micrographs at magnifications of 1000 ×. The bonding strength tests were carried out according to [11].

3. Results and discussion

Fig. 1a shows that the ternary Mg–1.2Ca–3Zn alloy consists of α-Mg and Ca₃Mg₆Zn₃ or MI (Ca₃Mg₆Zn₃₁₋ₓ, 4.6 ≤ x ≤ 12) according to Islam et al. [12] which is consistent with the Mg–Ca–Zn phase diagram [13]. The presence of secondary phases can significantly affect the corrosion behavior of the Mg alloy due to the formation of micro-galvanic cells between the matrix and secondary phases [14]. The EDS analysis showed that triple junction between the grains boundaries were enriched with zinc and calcium thus, indicating the formation of Ca₃Mg₆Zn₃ (Fig. 1d). The surface of the single-layered NiCrAlY coating is uneven and contains a certain level of roughness. It can also be observed that the underlayer contains a large amount of pores, voids and micro cracks due to the induced residual stresses from the deposition process (Fig. 1b) [15]. However, dual-layered NiCrAlY/nano-YSZ coating showed fewer amounts of pores and micro cracks. The corresponding EDS analysis result can be also observed (Fig. 1c). The semi-molten particles (SM) and molten particles (M) are also shown in Fig. 1c and e. It is reported that the semi-molten particles contain porous structure, while molten parts bonded with each other forms a dense structure [16]. Nanostructured YSZ is also observed in Fig. 1c which is composed of nanosized particles that can be retained from the non-molten part of the powder [8]. This structure contains large amount of nano-pores with a wide range of sizes which has significant effect on the corrosion behavior of the plasma spray coated alloy. Di Girolamo et al. [17] demonstrated that pores with different sizes exist in nano-YSZ. Fine pores originated from gas entrapped in the molten droplets, while the coarse pores are produced by filling structural defects and pull-out effects during grinding and polishing. In this view, the flight path and the thermal history of the agglomerated particles in the plasma jet affect the coating microstructure. In this regard, the melting process is associated to both temperature distribution in the plasma jet and to the heat transfer to the porous agglomerates [18]. Thus, with a optimization process the level of nanozones embedded in the coating microstructure which has significant effect on the corrosion and mechanical properties of the coated samples can be monitored [19]. The XRD results of the ternary Mg–1.2Ca–3Zn alloy show that the uncoated alloy consists of α-Mg and Ca₃Mg₆Zn₃ which is consistent with the SEM/EDS results. The NiCrAlY coating contain γ phase (Ni, Cr-rich), γ’ phase (Ni₃Al), AlCr₃ and some traces of β phase (AlNi) peaks. However, nanostructured YSZ include the tetragonal zirconia (t) only which can be attributed to rapid solidification during the process of APS (Fig. 1f).

Fig. 2a shows cross-sectional SEM image of the NiCrAlY coated Mg alloy sample, indicating large amount of voids, globular porosities and micro-cracks with different sizes. However, YSZ shows bimodal structure consisting of lamellar structure with columnar grains, which are surrounded with partially molten parts of the nanostructured powders and some equiaxed grains (micro- and nano-sized). In this regard, Di Girolamo et al. [20] showed the lamellar structure consisted of lamellae almost parallel to interface of the coating substrate, separated by splat boundaries and embedded in a network of cracks and voids. Formation of columnar grains can be due to the solidification of the melted part of the powder [21]. As can be seen that the dual-layer coating includes less linked pores, voids and micro-cracks because of the compactness of the nanostructured YSZ compared to single-layer coating. This leads to less infiltration of corrosive media to the Mg substrate (Fig. 2b). Single-layer NiCrAlY coating exhibited higher porosity (16–18%) compared to the dual-layer YSZ/NiCrAlY coatings (11–13%) hence, dual-layer coating is denser than that of single-layer coating. The molten and semi-molten regions, as one of the source of porosity in APS nanocoating, could be controlled by adjusting the feedstock characteristics [19,22].
addition, the porosity in the single-layer coated sample is much larger than that in the dual-layer coating. The presence of this coarse porosity in the single-layer coating caused more penetration of corrosive species to the substrate. Fig. 2c and d shows EDS elemental maps of the cross-sectional NiCrAlY and NiCrAlY/nano-YSZ coating samples, indicating formation of
NiCrAlY with a thickness of around 80 μm and YSZ layer with thickness of 270 μm as an underlayer. It seems that there is strong adhesion between the deposited coating and the underlying substrate. Fig. 3 shows TEM micrographs of NiCrAlY/nano-YSZ coating indicating the equiaxed grains with different sizes in the range of 30–80 nm. Similar result was also found by Wang et al. [23]. The orientation and size of these crystals strongly depend on the thermal condition during spreading of droplet [24].

The electrochemical polarization curves of plasma spray coated and uncoated showed that the corrosion potentials ($E_{corr}$) of the uncoated Mg–1.2Ca–3Zn, NiCrAlY and NiCrAlY/nano-YSZ coated samples were $-1638.7$ mV$_{SCE}$, $-917.3$ mV$_{SCE}$ and $-829.6$ mV$_{SCE}$, respectively (Fig. 4a). The more negative corrosion potential of the uncoated Mg–1.2Ca–3Zn compared with the coated alloy is due to the formation of a microgalvanic cell between α-Mg and the ternary secondary phase. However, single and dual-layered coating samples presented more positive $E_{corr}$ than uncoated sample. According to the mixed standard electrode potential theory [25,26], it was found that the air plasma spray coated samples were nobler than the uncoated Mg alloy. The corrosion current densities ($i_{corr}$) of the uncoated, single-layer and dual-layer coated samples were 217.1, 114.5 and 82.4 μA/cm$^2$, respectively. Both coated samples exhibit a lower $i_{corr}$ than the uncoated sample indicating lower corrosion rates of plasma sprayed coating samples. This can be attributed to the formation of a thick coating that leads to delaying the contact between the corrosive species and Mg substrate. Fig. 4b shows the Nyquist plots of uncoated and coated Mg samples thus, indicating a single capacitive loop at all high frequencies. The charge transfer resistance ($R_t$) of the coated samples are almost the same; however, the NiCrAlY/nano-YSZ coated sample showed higher polarization resistance (2502.2 Ω cm$^2$) than NiCrAlY coated sample (2199.2 Ω cm$^2$). The uncoated sample exhibited the lowest polarization resistance of 1437.1 Ω cm$^2$. This can be due to the protective nature of chromium and nickel, as well as the homogeneous coating composition [25].

More so, the dual-layered coated sample demonstrated larger loop diameter compared to the single-layered coated sample. This can be attributed to the formation of more compact coating and presence of lesser amount of pores, voids and micro cracks [27,28]. Microhardness value of uncoated alloy was 65.2 Hv and this value significantly increased to 210.4 and 760.8 Hv after NiCrAlY and NiCrAlY/nano-YSZ plasma spray coating respectively (Fig. 4c). This indicates that the dual-layered coating is approximately 12 times harder than that of the uncoated alloy. The higher hardness values of nano-YSZ coating compared to the NiCrAlY coating is due to the presence of semi-molten nanostructured particles that are embedded in the YSZ structure, which act as crack arresters thereby, increasing coating toughness [18,19]. In NiCrAlY coating, a crack propagates via the coating's weakest link, which is the well-defined layered structure such as the splat boundaries. Fig. 4d shows that the bonding strength of the dual-layer NiCrAlY/nano-YSZ coating is about 14.9 MPa which is slightly higher than that of single-layer NiCrAlY coated Mg alloy (12.8 MPa). Higher bonding strength of dual-layer coating can be due to better splat-to-splat contact obtained when using a nanostructured powder, which would also hinder crack propagation. This is also related to the crack arresting effect by the dense nanozones which enhances the bonding strength [18,19].

4. Conclusions

In this study, plasma sprayed NiCrAlY and NiCrAlY/nano-YSZ duplex coatings were deposited on Mg–1.2Ca–3Zn alloy with the aim of reducing corrosion rate. The nanostructured YSZ overlayer, compared to the NiCrAlY underlayer contains lower amounts of porosities and micro-cracks. The microhardness of the uncoated samples was found to significantly increase from 65.2 to 760.8 Hv after NiCrAlY/nano-YSZ plasma spray coating. However, NiCrAlY coating showed lower bonding strength compared to the NiCrAlY/nano-YSZ coating. Single-layer NiCrAlY and dual-layer NiCrAlY/nano-YSZ plasma spray coatings decreased the corrosion current density of the Mg–1.2Ca–3Zn alloy.
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References


