



Role of CeO₂ doping on tribological behavior of Al₂O₃ coated AZ91 alloy

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ABSTRACT

Ceramics inherently shows resistance against corrosion and wear by owing tremendous mechanical and thermal properties. Therefore, ceramics provide a solution to the various industrial problems arising due to material deterioration generally by wear or corrosion. Al₂O₃, due to its exceptional quality of good wear resistance, is deposited onto AZ91 alloy. Further, the role of rare earth oxide, i.e., doping of CeO₂ in Al₂O₃ coating, is also investigated. The surface and interface properties were evaluated using nanoindenter, scanning electron microscope, X-ray diffraction techniques and Goniometer. The tribological behavior of the coatings was observed by conducting sliding wear study under the reciprocating module. It was observed that the doping of CeO₂ contributed in lowering the coefficient of friction. The CeO₂ doping led to the refinement of coating microstructure and strengthening the substrate-coating interface as well. The improvement in mechanical and tribological properties in CeO₂ doped coatings can be attributed to the formation of CeO₂ and suppression of M-O phase as revealed during X-ray diffraction.

1. Introduction

Mg alloy has potential to find its use in various applications such as automotive [1, 2], aerospace [3, 4], electronics [3] and biomedical [5–7] industries. The properties like good castability, high specific strength [8], low density [1], etc. promote their use in various industrial applications. However, their use is limited due to their poor wear and corrosion resistance. Surface technologies such as chemical vapor deposition (CVD) [9, 10], physical vapor deposition (PVD) [9–11], electro-deposition [12, 13], micro-arc oxidation [12, 14], thermal spray [15, 16], cold spray [16, 17] have been developed to extend their use by deposit of various coatings. Among various surface modification processes, thermal spray is one of the efficient processes to deposit the various coatings; metallic, ceramic, cermet, etc. over a range of substrate. The diversity of this coating, i.e., to deposit numerous coatings on to wide range of substrate has increased its demand and dependency in the industrial sector to solve various engineering problems. This technology is used to enhance the service life and performance of the components which are in service under severe environment and leads to the deterioration using wear, corrosion, erosion, etc. [18]. Ceramic coatings can provide a solution to these industrial problems, especially, Al₂O₃ based coatings possess high stability to chemical attack, high hardness, and refractoriness which make them suitable for wear and corrosion resistant applications [12, 19]. Further,

D-gun technique is one of the suitable thermal spray technique to deposit the ceramic coatings onto the substrate with low porosity, high bond strength and hardness [20–22]. In an investigation made by Wang et al. it was observed that deposition of a ceramic coating on Mg alloy gives rise to increase in hardness and anti-corrosion property [23]. Al₂O₃ satisfies the requirements in various industrial problems occurring due to wear since its capability to combat it. In an investigation made by Saravanan et al. [24], the D-gun sprayed Al₂O₃ coating consistently exhibited the uniform microstructure along with the improved mechanical and superior tribological properties.

Moreover, it is reported that addition of rare earth oxides, to coatings, in a small amount can contribute in the enhancement of the coatings properties by various mean such as microstructure refinement, increase in hardness and beyond that improvement in other mechanical and tribological properties also [25, 26]. Rare earth elements are doped in protective coatings to improve their properties and combat against wear and corrosion under harsh service conditions [27]. In a study investigated by Xu et al. [28] it was reported that the addition of rare earth element in small amount inhibit the cracking/spallation of the coating during oxidation cycle also. Zhang et al. [27] investigated mechanical and tribological studies on CeO₂ doped and undoped Ni-based alloy coated steel substrate, and it was observed that CeO₂ doping led to the refinement of microstructure with purifying effects along with improvement in wear resistance of the coating. In another study

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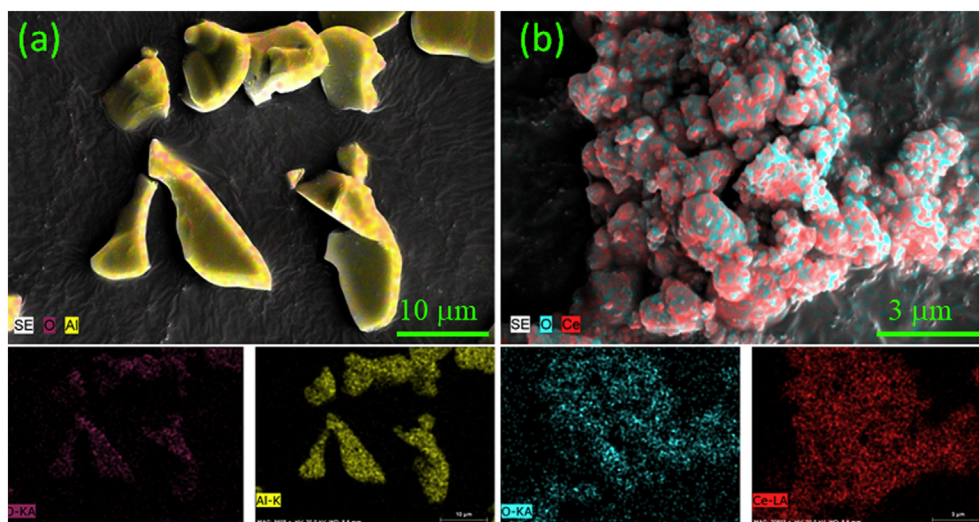


Fig. 1. SEM micrograph of (a) Al_2O_3 and (b) CeO_2 powders along with corresponding X-ray mapping.

carried out by the He et al. [25], CeO_2 was doped in $\text{Al}_2\text{O}_3/\text{Ni}$ based coating and it was observed that CeO_2 improved the microhardness, fracture toughness and reduced the porosity of the coating which ultimately played a role in enhancing the wear resistance by identification of two phases, i.e., Al_2O_3 hard phase; for increase in hardness and CeO_2 ; for grain refinement.

In a lubricated tribology contact, solid-liquid interaction plays an important role in controlling the tribological performance [29]. The literature lacks in correlating the tribological study with wetting and surface energy phenomenon. On the other hand, the rare earth has been proved to improve the hydrophobicity of the surfaces due to their unique electronic structure which doesn't allow the hydrogen bonding with interfacial water molecules [30].

The current study deals with the deposition of Al_2O_3 and CeO_2 doped Al_2O_3 coatings on solution treated AZ91 alloy using D-gun thermal spray technique and estimation of their mechanical, tribological and microstructural properties using nanoindenter, tribometer, SEM/EDS and XRD. The sliding wear study was conducted under reciprocating module in lubricated conditions. The study aims to test the sustainability of Al_2O_3 and CeO_2 doped Al_2O_3 ceramics coatings under tribological applications.

2. Materials and methodology

The substrate materials selected to conduct the study were AZ91 (Mg-9 wt%Al-1 wt%Zn) Mg alloy and near eutectic Al-Si alloy (Al-11.3 wt%Si-0.7 wt%Fe-1.8 wt%Cu-0.2 wt%Mn-0.6 wt%Zn-0.2 wt%Mg) and procured from Xi'an Yuechen Metal Products Co., Ltd. China and Ye Chiu, Malaysia respectively. The Al_2O_3 (99.5% purity) and CeO_2 (99.9% purity) powders were procured from Sigma Aldrich Chemical Pvt. Ltd., Bangalore, India. The Servo, Super 20W-40MG (SAE 20W-40) engine oil was used to provide the lubrication to the tribo-pair. The samples having dimensions $10\text{ mm} \times 9\text{ mm} \times 8\text{ mm}$ and $40\text{ mm} \times 20\text{ mm} \times 6\text{ mm}$ were EDM wire cut from the block of AZ91 and near eutectic Al-Si alloys respectively. Further, the samples were polished using 600, 800, 1200 and 2400 grit size emery paper followed by the cloth polishing using Al_2O_3 suspension having particle size $1\text{ }\mu\text{m}$. The samples were ultrasonically cleaned in ethanol and hot dried to remove any foreign impurity (if present).

2.1. Preparation of ceramic coatings

The coating was deposited using Al_2O_3 and 0.8 wt% CeO_2 doped Al_2O_3 powder as feedstock. The $\text{Al}_2\text{O}_3 + 0.8\text{ wt}\%\text{CeO}_2$ doped powder

was ball milled (60 rpm) for 8 h to obtain the homogenous composition. The steel balls having 2.5 mm dia were used in a ball mill and ball to powder ratio was kept as 1:2. Before deposition, the polished samples were grit blasted to enhance the substrate – coating interfacial strength. The surface roughness recorded after the grit blasted was around 5–6 μm . The coating was deposited using D-gun spray technique with process parameters as; standoff distance – 150 mm, firing rate – 3 shots/s, coating thickness per shot – 25–30 μm . The coatings were deposited at SVX 'M' Surface Engineering, Noida, India.

2.2. Characterization of the coatings

The Al_2O_3 and 0.8 wt% CeO_2 doped Al_2O_3 coatings were mechanically and microstructurally characterized using nanoindenter (Universal nanomechanical tester, UNAT, ASMEC), scanning electron microscopy: SEM (Zeiss EVO-MA 10) with energy dispersive spectroscopy: EDS (BRUKER, QUANTAX 70) and X-ray diffraction: XRD (Rigaku Ultima IV). The tribological behavior of the coatings was examined under tribometer (UMT 2, CETR). The selection of 0.8 wt% CeO_2 was made by optimizing the CeO_2 concentration as reported in our previous publication [31].

The nanoindentation study consisted the load of 30 mN with a loading rate of 2 mN/s. Before indentation, the coated samples were polished down to 2400 grit size emery paper followed by the cloth polishing using oil-based diamond suspension having particle size $1\text{ }\mu\text{m}$. The minimum distance between the successive indentation was kept at least 25 μm . Average of at least 15 indents were calculated and reported.

The tribology studies were conducted with a pin on flat configuration under the three different normal loads, i.e. 20 N, 30 N and 40 N with two different average velocities of 0.05 m/s and 0.2 m/s. The tests were performed under reciprocating module in lubricated conditions at room temperature. The duration of each test was kept 1 h and performed thrice.

3. Results and discussion

3.1. Morphology and microstructure

The powder morphologies of Al_2O_3 and CeO_2 powders are shown in Fig. 1. It can be observed that the Al_2O_3 powder consisted the particles of irregular and mixed shape whereas CeO_2 powder consisted globular shape.

Further, the as-sprayed morphology of Al_2O_3 and $\text{Al}_2\text{O}_3 + 0.8\text{ wt}\%$

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