ABSTRACT

Steel is extensively used in many industries, including automotive, petrochemical, food processing, biomedical, and aerospace, due to its cost-effectiveness, strength, hardness, biocompatibility, wear and corrosion resistance characteristics. However, it has limitations in extreme environments. Austenitic stainless steels, like SS304, are preferred in such extreme environments, but they degrade under intense corrosive and wear conditions. Hence, these surface/sub-surface degradations of SS304 steel can be eliminated by developing a new novel material. Nowadays, a novel category of alloys known as Multi-principal Element Alloys (MPEAs) has garnered significant interest from the scientific community owing to their multifunctional features. This study focuses on developing a novel TiNbMoMnFe-based MPEA using bulk fabrication and surface coating techniques. The performance of the developed MPEA and the coating are benchmarked with the responses of the SS304 steel.

The present research has been classified into three sections: (i) the development of bulk MPEA using microwave sintering, (ii) the development of MPEA coating using the High-velocity oxy-fuel (HVOF) thermal spray process, and (iii) exploring the effect of heat treatment on HVOF sprayed MPEA coating properties. Further, the metallurgical (XRD, FESEM, Raman, XPS, etc.), Mechanical (Hardness), Physical (Density, Porosity, Surface wettability), Tribological (Friction, Wear), and Electrochemical (Corrosion) characteristics of the bulk MPEA, MPEA coating, and heat-treated MPEA coating were studied and established the role microstructural changes on their superior properties.

Initially, the TiNbMoMnFe-based bulk MPEA was fabricated using the microwave sintering-assisted powder metallurgy technique. The MPEA powder was initially synthesized using a mechanical alloying technique. The optimal composition of the alloyed powder was further compacted into green pellets and then microwave-sintered at different temperatures. The exact single phase (BCC: TiNbMoMnFe) MPEA evolved at 1400 ºC. While sintering at less than 1400 ºC resulted in multiphase (BCC, FCC) MPEA. Thus, developed single-phase (TiNbMoMnFe) MPEA exhibited a hardness of $\approx$ 16 GPa and porosity of around 8%. The tribological exploration suggested that the multiphase alloys (sintered at 1100 ºC - 1300 ºC) are prone to adhesive wear followed by oxidative wear. Due to high hardness, the single-phase MPEA underwent minimal plastic deformation and some surface abrasion. This also resulted in the exposure of nascent surfaces, leading to oxidative wear. Hence, the wear resistance was increased by $\approx$ 54%. The single-phase MPEA (BCC: TiNbMoMnFe) showed excellent

corrosion resistance (Corrosion rate: ≈ 99% reduction for short-term exposure, ≈ 83% reduction for long-term exposure) attributed to the lack of high-energy sites and the formation of a stable and continuous passive layer on the surface.

The SS304 steel-facing surface/sub-surface degradations can be projected by developing the MPEA coating. The TiNbMoMnFe-based MPEA coating on SS304 steel was developed using the HVOF thermal spray process. This study investigated the role of feedstock powder preparation on the overall coating performance. The MPEA coatings were developed by preparing the feedstock powder at different time scales, 5 h, 10 h, and 15 h, respectively. Among them, the 15 h milled MPEA coating exhibited a very dense and homogeneous structure with low porosity (≈ 1%), superior surface finish (Ra ≈ 2.57 μm), and hardness (≈ 13 GPa). Tribological studies under dry sliding conditions revealed that the 15 h milled MPEA coating was highly wear-resistant compared to other coatings (86% reduction). For long-term exposure to simulated body fluid (SBF), the MPEA coating showed much-improved anticorrosion performance (corrosion rate reduced by ≈ 98%). The dual protective mechanism involved the formation of a TiNbMo-rich passivating layer and apatite deposition on the surface during long-term exposure. Long-term exposure to NaCl medium,15 h MPEA coating recorded a ≈ 99.5% reduction in corrosion rate after 5 weeks. The protective mechanism was associated with the formation of a TiNbMo-rich passivating layer. However, the SS304 substrate was prone to severe corrosion. The erosion studies suggested that the failure mode was ductile. The 15 h milled MPEA coating showed an ≈ 88% reduction in erosion rate at a 30º impingement angle.

The 15 h milled MPEA coating was further heat-treated at 700 ºC, 900 ºC, and 1100ºC and studied the effect of heat treatment on the mechanical, metallurgical, corrosion, and tribological properties. Heat treatment made the coating denser, more compact, and less porous. Upon heat treatment, the single-phase BCC structured as-sprayed MPEA coating transformed to dual-phase (BCC and FCC) MPEAs, and the presence of the FCC phase dominated over the BCC phase when heat treated at 1100 ºC. The 900 ºC heat-treated coating showed the highest nano and scratch hardness due to the dual-phase behavior, and hardness started degrading after 900ºC. Also, the 900 ºC heat-treated coating had excellent wear resistance; the major wear mechanism was abrasive wear followed by oxidative wear. Similarly, the 900 ºC heat-treated MPEA coating had the highest corrosion resistance (≈ 92% reduction). Hence, the particular composition is not recommended for heat treatment beyond 900 ºC