## Development of Fe based Metallic Glass Composite Coating by HVOF Spraying: Optimization of Corrosion and Wear Resistance

## ABSTRACT

In recent times, Fe-based metallic glass (MG) coatings prepared by different thermal spraying techniques are being investigated as a potential candidate for surface protection of various structures attributed to their remarkable combination of mechanical and chemical properties, including, superior strength, high hardness and outstanding wear and corrosion resistance. Despite of these appealing properties, the application of monolithic MG coatings is hindered gravely due to their inherent room temperature brittleness. Alternately, the preparation of MG composite coating has proved to be an effective approach to enhance the toughness owing to the hindrance to shear band propagation and promotion of multiple shear band formation caused by the crystalline phases.

Accordingly, in this Ph.D. thesis work, Fe-based MG composite coatings were synthesized using two lean compositions devoid of costly elements, such as Y, Nb, Hf, Ni, etc., Fe<sub>63</sub>Cr<sub>9</sub>B<sub>16</sub>C<sub>7</sub>P<sub>5</sub>, at. % (Powder-1) and Fe<sub>57</sub>Cr<sub>9</sub>Mo<sub>5</sub>B<sub>16</sub>C<sub>7</sub>P<sub>6</sub>, at. % (Powder-2, with minor Mo) via high velocity oxy-fuel (HVOF) spraying with different powder feed rates to vary the heat input. The correlation between the combined effect of porosity and amorphicity, resulting from melting through varying the heat input during HVOF process on corrosion and mechanical (hardness and wear) properties of the coatings have been investigated extensively. Microstructural and phase analyses revealed that amorphicity of the coating increased, whereas porosity content decreased gradually with the increment in feed rate, associated with the reduced degree of melting of powder particles and the HVOF shot peening effect, respectively. The retention/formation of amorphous phase in the coatings was attributed to the high glass forming ability of the feedstock powders and relatively higher cooling rate of the HVOF spraying process.

Improving the corrosion resistance and meanwhile maintaining superior mechanical properties (hardness and wear) of HVOF sprayed MG composite coating is challenging because of the conflicting role of crystallization on wear and corrosion resistance. Therefore, optimization of the process parameters was carried out, and Powder-1 based coating synthesized with higher feed rate exhibited enhanced corrosion as well as wear resistance, attributed to a better combination of porosity and amorphicity. The enhanced corrosion resistance at higher feed rate was ascribed to the presence of higher content of protective phases (chromium hydroxide and Cr substituted hematite) in the corrosion products. Besides, the improved mechanical and wear properties at elevated feed rate were due to the reduction in volume fraction of softer nanocrystalline  $\alpha$ -Fe phases (higher amorphicity) and better intersplat bonding (lower porosity).

Defects such as porosity and crystallization are inevitable in thermal sprayed MG coatings, which are introduced during the synthesis process, and the corrosion behavior of these coatings is adversely affected by the presence of such defects. However, the identification of a particular

microstructural defect among crystallization and porosity to have a greater influence on the corrosion resistance of thermal-sprayed Fe-based MG composite coating has remained elusive so far. Thus, to address this issue, two melt-spun ribbons with no porosity having different amorphous content were synthesized, viz. (i) fully amorphous and (ii) partially amorphous structure with similar amorphicity as that of the coating. Electrochemical characterization results revealed a greater influence of the reduced amorphicity on the corrosion behavior than that of the porosity in the fully amorphous matrix. Moreover, results of Raman analysis and Auger electron spectroscopy revealed that fraction of protective phases in the corrosion products, depletion of Cr and thinning of passive film were significantly affected by crystallization of amorphous structure, compared to additional porosity effect. These results revealed reduced amorphicity as the primary factor that affects the corrosion behavior of such coatings, and a mechanism has been proposed to explain the role of amorphicity and porosity on the corrosion behavior.

Besides, the influence of minor amount of Mo addition on corrosion and wear properties of the coating was investigated. The coatings were prepared using optimized deposition parameters for eliminating the porosity effect and to only investigate the influence of Mo addition. Powder-2 based (minor Mo) coating exhibited an enhanced corrosion resistance, ascribed to the improved passivation ability resulting from increased fraction of protective and stable Cr- and Mo-oxides in passive film. Moreover, a superior wear resistance was also observed, because of increment in amorphous content and minor amount/absence of softer  $\alpha$ -Fe phases. Thus, the addition of a minor amount of Mo was observed to be advantageous for improving the wear and corrosion properties of this Fe-Cr-based MG composite coating.

Further, the transition in wear behavior as a function of applied load, reciprocation speed and longterm exposure in MG composite coating has not been clarified yet. Accordingly, reciprocating wear behavior of Powder-2 based coating was investigated under different load, speed and distance. Specific wear rate revealed an increasing trend with both load and speed; however, this variation in wear rate was more significantly affected by the change in speed rather than the load. Moreover, the wear properties exhibited an insignificant change with the increment in sliding distance. The evolution of load, speed and distance dependent wear behavior of the MG coating was correlated with the transition in wear mechanisms.

Interestingly, both the MG composite coatings exhibited improved corrosion and wear resistance than that of SS316L coating synthesized with industrially optimized parameters, insinuating their effectiveness as inexpensive surface protective coatings. This work will ultimately help in the development of inexpensive Fe-Cr-based MG composite coating possessing enhanced corrosion and wear resistance.

**Keywords:** Fe-based metallic glass composite coating; High velocity oxy-fuel spraying; Microstructural and compositional heterogeneities; Multi-scale indentation and wear; Corrosion behavior evolution; Passive film; Corrosion degradation mechanism; Reciprocating dry sliding wear behavior; Transition in wear mechanism