Announcing the Final Examination of Virendra Singh for the degree of Doctor of Philosophy

Time & Location: January 18, 2012 at 11:00 AM in 151 AMPAC 120
Title: Rare earth oxide coating with controlled chemistry using thermal spray

Cerium oxide (Ceria)-based material at nano scale has been gaining significant attention due to its numerous technological applications. Ceria in both doped and undoped forms are being explored as oxygen sensor, catalysis, protective coating against UV and corrosion, solid oxide fuel cell (SOFC) electrolyte and newly discovered antioxidant in biology. Additionally, rare earth elements or their oxides improve corrosion and oxidation resistance of the alumina- and chromia- forming alloy due to the reactive element effect. Thus, there is an imminent need of a technology which can provide a cost effective, large scale nano-manufacturing of nano ceria consolidation e.g. thermal spray.

This dissertation targets the scientific understanding and development of pure and doped ceria- based coating for a variety of technological applications, from SOFC to corrosion resistant coating. Atmospheric plasma spray (APS) and solution precursor plasma spray (SPPS) techniques for the fabrication of nano ceria coating were investigated. A spray drying technique was used for the agglomeration of nano particles to achieve high density nano-structure coating in plasma spray. The physical properties of the agglomerates and large number of interrelated process variables makes ceria deposition complex. Thus, deposition efficiencies of the coatings and porosities level as a function of processing parameters were analyzed and optimized using statistical design of experiments. The coating deposition efficiency was found to be greatly dependent on the plasma temperature and vaporization pressure of the ceria particles. However, low standoff distance and high carrier gas flow rate were responsible for the improved density upto 86 ±3%. An alternative novel SPPS technique was studied for thin cerium oxide deposition from various cerium salt precursors in doped and undoped conditions. The SPPS process allows a controlled chemistry of coating at molecular level for tailored applications. The deposition mechanism by single scan experiments and effect of various factors on coating microstructure evolution were understood in term of splats formation. It was found that the precursor salt (nitrate of cerium) with lower thermal decomposition temperatures was suitable for high density coating and validated by thermodynamic calculations. The high concentration and low spray distance significantly improve the splat morphology and reduce porosity (upto 20%).

The feasibility of the trivalent cations (Sm 3+ and Gd 3+) doping into cerium oxide lattice and non-stoichiometry in high temperature plasma was experimentally studied and proved by XRD and XPS analysis. Due to facial switching between Ce4+ and Ce3+ oxidation state, the cerium oxide surface becomes catalytically active. Thus, the air plasma sprayed ceria coated 17-4PH steel was investigated for their applicability under extreme (high pressure (10Kpsi) and temperature (300 oF)) corrosive environment. The coated steel showed continuous improvement in corrosion resistance at 3.5wt% NaCl at ambient temperature for 3 months study whereas, high pressure did not reveal significant role. The ceria coated steel also revealed the improvement in corrosion protection (by 4 times) compared to bare steel at low pH, 300F and 4000Psi environment.

Nevertheless, the extensive TEM, SEM, XRD, TG-DTA and impedance spectroscopy were conducted to evaluate the precursors, coating microstructure and corrosion.

Major: Material Science and Engineering

Educational Career:
Bachelor's of Metallurgical Engineering, BS, 1999, MNIT, India
Master's of Metalurgical Engineering, MS, 2003, Indian Institute of Science, India

Committee in Charge:
Dr. Sudipta Seal, Chair, AMPAC
Dr. Kevin Coffey, MMAE
Seetha Raghavan, MMAE
Helge Heinrich, MMAE/Physics
Lei Zhai, Chemistry/NSTC

Approved for distribution by Dr. Sudipta Seal, Committee Chair, on January 1, 2012.

The public is welcome to attend.