ABSTRACT

To establish pyrochemical reprocessing plants for reprocessing of spent metallic fuels of Fast Breeder Reactors with various unit operations it is necessary to identify, develop and qualify reliable corrosion resistant materials and coatings for service in molten LiCl-KCl salt and molten uranium environment operating between 773 to 1573 K. Carbon based materials are proposed as candidate materials for salt purification and cathode processor crucibles, vessels and liners in pyrochemical reprocessing involving molten LiCl-KCl salt medium and molten uranium. The present thesis work is focused on evaluation of materials and coatings for salt purification system crucible where molten LiCl-KCl salt will be handled and for the cathode processor crucible where the combined environment of 20 wt% molten salt, cadmium and molten uranium is present. To meet the requirement of pyrochemical reprocessing unit operations, the evaluation and performance of materials and coatings were studies in molten LiCl-KCl salt at 873 K for 2000h as well as in molten uranium at 1623 K. The corrosion behaviour of the carbon materials viz. low density graphite (LDG), high density graphite (HDG), glassy carbon (GC) and pyrolytic graphite (PyG) was investigated in molten LiCl-KCl electrolyte salt medium at 873 K for 2000 h under ultra high pure (UHP) argon atmosphere for selecting the material for salt purification crucible application. Morphological changes in the carbon materials exposed to molten LiCl-KCl salt revealed severe corrosion attack on LDG and HDG and the attack on GC was insignificant due to non-penetration of salt into GC. Removal of carbon particles and surface degradation were not found in PyG exposed to molten LiCl-KCl and these are observed in LDG and HDG. The corrosion
resistance of carbon materials in molten LiCl-KCl salt at 873 K was observed to follow the order: LDG < HDG < GC < PyG.

Owing to its availability and economic viability, HDG is considered as one of the structural materials for salt purification system and as cathode processor crucible. The performance of HDG in molten LiCl-KCl salt clearly indicated that ceramic coatings are desirable on HDG components (crucibles) in order to protect them from corrosion attack by salt and molten uranium and to extend their service life and mechanical integrity at high operating temperatures. Hence, ceramic coatings of partially stabilized zirconia (PSZ) with NiCrAlY bond coat and top alumina-40 wt% titania (A40T) with bond coat of Cr$_3$C$_2$-NiCr and without bond coat were developed on HDG substrates by plasma spray process and these were evaluated for deploying these coated materials for crucible, liners and vessels applications in pyrochemical reprocessing. The ceramic coated HDG samples were exposed to molten LiCl-KCl salt for 2000 h at 873 K under UHP argon atmosphere and compatibility test with molten uranium at 1623 K for 20 min under UHP argon atmosphere. The unit operations of salt purification and cathode processor are batch processes in pyrochemical reprocessing. Hence, the durability of coatings developed on HDG substrate need to be evaluated. For this purpose, ceramic coated HDG samples were subjected to thermal cycling to understand the durability of the coatings. The molten salt tested carbon materials and ceramic coated HDG (as-coated and tested) samples were characterized by Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), Atomic force microscopy (AFM), X-ray diffraction (XRD) and Laser Raman spectroscopy (LRS).

The A40T coating developed cracks and salt deposits were found after exposure to molten salt for 500 h and spallation of A40T coating occurred from HDG substrates after
2000 h of exposure with Cr$_3$C$_2$-NiCr bond coated as well as without bond coat. To improve the performance of A40T coating in molten salt, post treatments (annealing and laser melting) were performed. It is evident from the results that denser and compact microstructure can be obtained by pulsed laser melting as compared to vacuum annealing of coatings. Laser melted A40T coatings were exposed to molten salt showed that the laser melted coatings exhibited better corrosion resistance owing to their fully dense top layer. The PSZ coated HDG exhibited excellent corrosion resistance in molten LiCl–KCl salt due to good adherence of the coating to the substrate even after 2000 h of exposure and no change in the morphology as well as in the phases of the PSZ coating was observed.

For selecting a coating for cathode processor crucible, the studies were carried out for testing the PSZ coated samples with molten uranium at 1623 K. A40T coating exhibited poor adhesion on graphite surface and spallation of coating was observed after compatibility test with molten uranium in addition to the adherence of uranium metal on the coating surface. The compatibility of molten uranium with PSZ coatings studies showed that PSZ coating protect the HDG, since the reaction products/layer observed on the surface of the coating was insignificant. A40T coated HDG with Cr$_3$C$_2$-NiCr and without bond coat samples were subjected to thermal cycling studies at 873 K exhibited complete coating spallation after 60 and 80 cycles respectively. The failure of A40T coating is due to the poor adhesion strength of the coating to the HDG substrates in both the cases. PSZ coated HDG subjected to thermal cycling studies at 873 and 1023 K showed that PSZ coating did not exhibit any failure of the coating even after 200 cycles and only network of cracks generated in the microstructures still resolved with stable tetragonal phase of the PSZ. The results of the studies reported in this thesis upheld the choice of HDG crucibles and PSZ coating on them for corrosion protection.
in molten chloride salt medium and molten uranium based on the performance in both the environments. Finally, PSZ coating was developed on engineering scale facility HDG crucibles for future studies at 1623 K to evaluate the combined (molten salt and molten uranium) environment effect on the coated crucibles.