Abstract

Stainless steel (SS) is the major structural and core components in many industries, which includes chemical, petrochemical, nuclear, sugar, paper and pharmaceutical. The components made up of SS often face the problem of wear, corrosion and fatigue under aggressive engineering conditions. In order to improve these properties, the method of hard facing or coating the metal with a hard material is commonly practiced. The carbides and nitrides of transition metals especially of Cr and Ti have such properties. Even though CrN and TiN exhibit hardness in the range 1000-2400VHN, CrN is preferred for the reasons that, it is stable at high temperatures, its coefficient of friction is equal to or less than that of TiN and hot air oxidation resistance is better than that of TiN. Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD) are the two techniques, which are widely used to produce CrN coatings. Among these two, CVD has many advantages, which include conformal coverage, uniform thickness and more throwing power. However, the success of any CVD lies in the proper choice, design and selection of precursors that can produce the metal atom in vapour phase.

The primary objective of the present investigations is to design and to synthesize low melting and volatile precursors of chromium and nickel. Determination of some of the relevant thermodynamic parameters like vapour pressure, heats of sublimation, fusion and vapourisation of the volatile complexes of Cr and Ni using a novel TG based transpiration technique forms the important part of the investigations. The other objective is to demonstrate that these can be cracked by plasma in situ with nitrogen carrier gas and can deposit CrN on to the SS and other substrates. The thesis also demonstrates the application of both the process and the precursors for the deposition of Ni either individually or as composite coatings with CrN and its complete structural and topographical description.

Several precursors encompassing organo-metallic, metallo-organic and nitrogen rich complexes were designed, synthesized and characterized in terms of thermogravimetric analysis as a screening tool. Of all these, Cr(acac)$_3$ and Ni[(acac)$_2$en] were chosen as the potential precursors as they vapourise completely without undergoing any decomposition and thus were opted for the present CVD applications. The standard enthalpy of sublimation for Cr(acac)$_3$ in
the temperature range of 374-418K yielded a value of 111.6±3.0 kJ/mol. The standard enthalpy of fusion was determined indirectly by a cryoscopical technique employing a non-volatile nickel solute to be 109.9±0.4kJ/mol. The standard enthalpies of sublimation, vapourisation and fusion of Ni[(acac)₂en] determined in the temperature range of 406-495 K were found to be 118.04±4.1, 83.34±3.8 and 34.7±4.0 kJ/mol respectively. This is the first report on such studies for the Ni complex, while for the Cr precursor the sublimation enthalpy corroborates with other techniques reported earlier in the literature.

A novel plasma assisted chemical vapour deposition technique was adapted and the process parameters were optimized for the production of CrN and Ni films. X-ray diffraction analysis was used to identify the structure and grain sizes of the deposited films. The films contained cubic CrN phase with a lattice parameter of 4.15Å. Hard CrN coating with hardness greater than 1000VHN and grain size of about ~10nm could be obtained at 823K. Scanning Electron Microscopy (SEM) demonstrated a dense, uniform and pore free microstructure and Energy Dispersive X-ray (EDX) analysis confirmed the presence of Cr and N in the film. Thick films of about 60 microns could be successfully developed on SS substrates. Difficulties of adhesion of these thick films were overcome by modifying substrate surfaces by grit blasting.

In order to reduce the thermal expansion mismatch between CrN and SS, the process conditions for the deposition of Ni films were established. The deposition for Ni films were performed at different substrate temperatures to obtain the desired uniform pore free surface morphology. Depositions performed at 723 and 823K exhibited films with pores, whereas at 873K uniform, fine grain, pore and crack free morphology were obtained. XRD confirmed the presence of nanosized nickel with traces of carbide in the films. Hardness measurements on these Ni films showed that they are soft compared to that of CrN films. Composite coatings of CrN and Ni were successfully developed at 823K by simultaneous deposition by taking the equal weight % of both the precursors. The EDX/SEM revealed the presence of Cr and Ni in the coatings. XRD analysis showed that the coating had biphasic mixtures of CrN and Ni with the nano sized particles. The addition of Ni to CrN reduces the hardness of CrN and makes it ductile. The co-deposition of Ni with CrN provides a new route to engineer superior mechanical and corrosion properties when compared to that of the bare stainless steel substrates or with CrN alone on SS.