

Microbially Induced Corrosion (MIC) of materials is a major concern of marine industry. Various ferrous and non-ferrous materials used in industry are prone to MIC. Bio-fouling or formation of bio-film on material surface is a precursor to MIC. Bacteria such as sulphate reducing bacteria (SRB) are most widely implicated in bio-fouling and MIC in marine environments. This work investigates bio-fouling, and its effect on electrochemical corrosion behavior of Ni-Ag nanomaterials in 3.5 wt. % NaCl. This dissertation is organised into three major parts (as described below) that focuses on synthesis of Ni-Ag nanomaterials and their corrosion behaviour before and after their exposure to a mixed culture of SRB.

The first part of the thesis describes synthesis, electrochemical behavior, biofouling and MIC of electrodeposited Ni-Ag alloy coatings on Cu substrate. Room temperature co-deposition from sodium citrate based electrolytic bath yielded two nanocrystalline Ni-Ag alloy coatings, namely Ni-7 at.% Ag and Ni-14 at.% Ag. The microstructure comprised of a Ni-rich fcc Ni-Ag phase and a Ag-rich fcc phase with comparable crystallite sizes of 19 and 16 nm respectively. Extent of solid solution between Ni and Ag was related to Ni-Ag crystallite size. The corrosion potentials of pure Ni, Ni-7 at.% Ag and Ni-14 at.% Ag coatings were -0.03 ± 0.005 V, 0.165 ± 0.004 V and 0.055 ± 0.003 V respectively. Ni-Ag alloy coatings demonstrated significant ennoblement of corrosion potential due to Ni-Ag solid solution. Percentage reduction in corrosion rate due to addition of 7 at.% Ag and 14 at.% Ag was 57% and 43% respectively. Upon exposure SRB, Ni-Ag coatings exhibited less bio-fouling compared to pure Ni coatings, and these bio-films essentially consisted of biogenic sulphides and hydroxides. The rate and extent of the bio-film formation decreased significantly with increasing Ag content. Greater resistance of Ni-Ag coatings to bio-fouling was related to ennoblement of the corrosion potential caused by Ni-Ag metastable phase. Galvanic coupling between Ni in the microstructure and biogenic sulphides in the biofilms contributed to MIC. The Ni-14% Ag coatings exhibited the least reduction in corrosion resistance due to bio-fouling while the pure Ni coatings and Cu substrate suffered significant losses in corrosion resistance. Similarly, reduction in the microbially induced corrosion rate of Ni due to addition of Ag was about 65%. This study revealed that Ni-Ag nanocrystalline materials are promising for control of MIC in marine environment.

This second part of the dissertation investigates electrochemical behaviour, biofouling and MIC of Ni-Ag nanocomposite coatings as a function of Ag content. Two Ni-Ag nanocomposite coatings with composition of Ni-0.25 at.% Ag and Ni-0.75 at.% Ag were electrodeposited on Cu by dispersing varying amounts of separately synthesised Ag nanoparticles into an aqueous bath of Ni⁺⁺ ions. Corrosion, Ni passivation and biofouling of Ni-Ag coatings were compared with the electrodeposited pure Ni coatings. Incorporation of Ag nanoparticles in electrodeposited Ni matrix produced significant change in the crystallite size, texture co-efficient and strain in the nanocomposite coatings. The corrosion potentials of pure Ni, Ni-0.25 at.% Ag and Ni-0.75 at.% Ag nanocomposite coatings were -0.05 ± 0.004 , -0.018 ± 0.004 , -0.019 ± 0.003 V respectively. Ni-0.25 at.% Ag showed the maximum corrosion resistance due to a favourable combination of largest crystallite size, texture along {111} family of planes, and negligible elastic strain. Addition of 0.25 at.% Ag and 0.75 at.% Ag resulted in 75% and 69% reduction in corrosion rates of Ni. Resistance to bio-fouling increased with Ag content confirming anti-bacterial properties of Ag nanoparticles. The reduction in the microbially induced corrosion rate of Ni due to addition of 0.25 at.% Ag and 0.75 at.% Ag was 72% and 79% respectively. Compared to Ni-Ag alloy coatings, Ni-Ag nanocomposite coatings exhibited remarkable resistance to bio-fouling and MIC establishing anti-microbial effects of Ag nanoparticles against SRB.

The third and last part of this dissertation explores interrelationship between electrochemical corrosion behaviour and anti-bacterial properties of chemically synthesised Ni-8.5 at. % Ag and Ni-20 at. % Ag nanoparticles. Rapid reduction of Ni⁺⁺ and Ag⁺ ions metal ions under highly non-equilibrium conditions led to the formation of a supersaturated single phase fcc Ni-Ag solid solution in both Ni-Ag nanoparticles. Particle size significantly decreased with Ag content revealing the inverse relationship between particle size and extent of Ni-Ag solid solution. This Ni-Ag solid solution gave rise to ennoblement of corrosion potential and reduction in the corrosion current density as compared to the pure Ni nanoparticles. The corrosion potentials of Ni, Ni-8.5 at.% Ag and Ni-20 at.% Ag were $-0.044 \pm 0.003\text{V}$, $0.145 \pm 0.004\text{V}$ and $0.256 \pm 0.003\text{V}$ respectively. Percentage reduction in corrosion rate of Ni due to addition of 8.5 at.% Ag and 20 at.% Ag was 69% and 82% respectively. While the pure Ni nanoparticles failed to inhibit the SRB growth, pure Ag and Ni-Ag nanoparticles brought about complete inhibition of SRB growth at nanoparticle concentrations of 15 mgL^{-1} and 50 mgL^{-1} respectively. Electrokinetic analysis of the Ni-Ag nanoparticles and SRB cells after their exposure to each other revealed the underlying mechanism for the antibacterial action. Interaction between SRB and Ni-Ag nanoparticles led to a significant shift in the isoelectric point of the SRB cells in the Zeta potential measurement. This confirmed the destructive chemical interaction between SRB cells and the Ni-Ag nanoparticles. Such destructive interaction was duly supported by observed unfavourable morphological changes in the SRB cells. Excellent anti-bacterial properties demonstrated by Ni-20 at.% Ag nanoparticles was found to be related to electrochemical ennoblement induced by Ni-Ag alloying. Based on careful analysis of the results obtained from the above studies, the following general conclusions can be drawn.

Electrodeposition and wet chemical synthesis are two effective routes to preparing Ni-Ag nanomaterials with tunable composition and microstructure. The amount of Ag in Ni-Ag nanomaterials can be closely controlled to achieve desirable electrochemical corrosion behaviour, and anti-microbial properties. Firstly, electrochemical corrosion of Ni-Ag nanomaterials can be primarily related to Ag content and Ni-Ag microstructure. Within the composition range studied, i.e. 0-20 at.% Ag, Ni-Ag was found to be more corrosion resistant compared to pure Ni either due to Ni-Ag solid solution or Ag-induced Ni texture in the Ni-Ag microstructures. Ni-Ag solid solutions were nobler than pure Ni, and consequently enhanced corrosion resistance of Ni-Ag nanomaterials. Such Ni-Ag alloying in Ni-Ag nanomaterials was favoured by small crystallite size compared to crystallite size in similarly prepared pure Ni. This explained the inverse effect of crystallite size on the corrosion resistance in Ni-Ag nanomaterials. In single phase Ni-Ag microstructures, corrosion resistance increased with Ag content due to Ni-Ag phase and absence of galvanic coupling. However, in the case of phase-segregated microstructure, corrosion resistance due to Ni-Ag phase was challenged by galvanic coupling between Ni-rich and Ag-rich phases. Extent of bio-fouling (or anti-microbial properties) of Ni-Ag nanomaterials decreased with Ag content regardless of whether the microstructure consisted of single Ni-Ag fcc phase or phase-segregated phase structure. Compared to pure Ni, both pure Ag phase as well as Ni-Ag fcc phase were found to resist the SRB growth due to electrochemical nobility thereof. Reduction in corrosion resistance, due to bio-fouling, of Ni-Ag nanomaterials decreased with increasing Ag content, indicating that microbially induced corrosion of Ni-Ag nanomaterials in chloride media can be controlled by reducing the extent of bio-fouling. It is equally important to note that toxicity of Ni-Ag nanomaterials in marine environment can be considered to be negligible based on low solubility of silver based compounds such as silver chloride, silver sulphide in marine water. It can be concluded that Ni-Ag nanomaterials with

tailored Ag content and microstructure can pave the way for an effective and eco-friendly approach for prevention microbially induced corrosion in marine environment.