Studies on Electrodeposited Ni-Composite Coatings Containing Cost-Effective and Exemplary Distributed Phases

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Abstract: In recent years, there is an enhanced interest in the development of electrodeposited Ni nanocomposite coatings containing distributive phases in the nanosize range for myriad applications in aerospace, automobile and engineering sectors. These coatings exhibit improved microhardness, corrosion resistance and wear resistance compared to plain Ni coating. The properties of the electrodeposited Ni nanocomposite coatings not only depend on the bath composition and electroplating parameters, but also the nature of the distributive phases. The present manuscript depicts how innovations made with respect to the distributive phases used in electrodeposited Ni composite coatings have resulted in some propitious Ni-composite coatings that are cost-effective and exhibit synergistic wear and corrosion-resistant properties. The unique features of different Ni-composite coatings explored in the author's laboratory are highlighted in this paper.

Keywords: Ni; Composite; Electrodeposition; Corrosion; Wear; Microhardness

1. Introduction

There is an increasing demand from industries for the development of superior surface coatings with higher wear and corrosion resistance for improved performance of engineering components [1]. Among the various surface engineering techniques, the electrodeposition method is highly promising due to its simple processing, cost-effectiveness, high productivity and homogeneity in composition. The electrodeposition conditions and plating bath influences the coating properties. Electrodeposited nickel possesses higher strength, improved toughness and wear and corrosion resistance and hence it is employed in a plethora of applications. To further enhance the coating properties, nickel-based composite coatings containing ceramic powders have been explored for combining the corrosion resistance and strength of nickel with the hardness, oxidation and wear resistance of ceramic particles and with the sole aim of achieving properties similar to hard chrome. To date, Ni–SiC is the only coating that is commercially exploited as a wear-resistant composite coating for rotary and reciprocating engines [2]. It is also employed for enhancing the corrosion resistance of magnesium alloys [2]. Nevertheless, the application of this coating above 400 °C is limited due to the formation of brittle silicide and thereby resulting in the degradation of the coating properties. Therefore, there is a need for replacement for SiC and oxide particles can substitute for SiC particles. During the first decade of 2000, oxide particles with the required sizes and compositions were not readily available in the Indian market and the imported oxides were expensive. The author's team employed oxide particles that were synthesized in the laboratory.

In the present study, solution combustion and coprecipitation synthesized nanosize oxide powders were effectively used for the development of electrodeposited Ni composite coatings possessing improved microhardness, corrosion and wear resistance. Naturally available cheaper volcanic rock (pumice), zircon and fly ash waste materials were used as distributive phases for electrodeposited Ni composite coatings. The indigenous preparation of nanosize oxides was scaled up in the laboratory (150 g/batch).

2. Experimental

Figure 1 depicts the overall work involved in the development of electrodeposited composite coatings. It involved the synthesis of distributive phases and Ni-sulfamate bath. The obtained electrodeposited composite coatings were evaluated for their mechanical properties and wear and corrosion resistant properties.

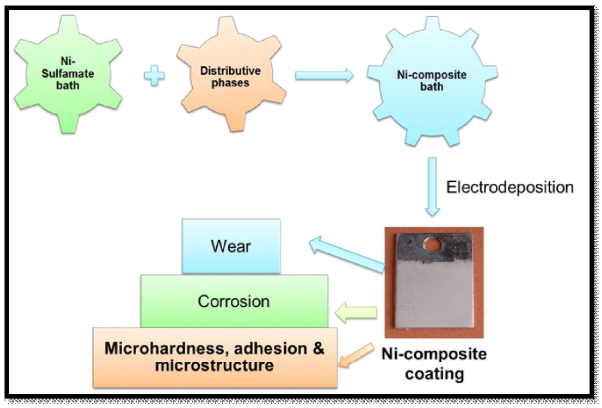


Fig.1. Schematic of the steps involved in the development of electrodeposited Ni-composite coating.

Generally, nickel coatings are developed by electrodeposition process using different types of baths [3]. The important baths are (i) Watts nickel plating solutions, (ii) nickel sulfamate solutions, (iii) all-Chloride solutions, (iv) sulfate-chloride solutions, (v) all-sulfate solutions, etc. In the present study, nickel sulfamate bath was used as nickel coatings deposited in nickel sulfamate bath possess the lowest internal stress. Besides, high nickel concentrations of sulfamate electrolytes permit to conduct electroplating at higher current densities (high rates of deposition). The object to be plated is maintained as cathode the nickel rod is used as the anode (Fig. 2). Positive ions flow from the anion towards the object being plated, through the plating solution (electrolyte), and finally deposit onto the surface of the object. The Ni^{2+} ions in the electrolyte that are attracted towards the cathode are replenished by the Ni^{2+} ions from the anode. For developing composite coatings, the particles to be incorporated in the coating were dispersed in the nickel sulfamate bath in various amounts and during electrodeposition, the particles were kept in suspension by stirring the contents of the beaker on a magnetic stirrer. The particles move towards the cathode and get electrophoretically deposited along with the nickel ions. The process of particle incorporation in the metal matrix during electrocodeposition may be described through the following steps: (i) particles transfer from the bulk of the solution to the metal surface, (ii) interaction i.e. adsorption of particles with the electrode surface and (iii) particle embedding in the growing metal matrix. For more details regarding the mechanism of electrodeposition, readers can refer to the seminal review articles by Hovestad [4] and Walsh [1].

The steps involved in the preparation of the nickel sulfamate bath are shown in Fig.2. The obtained nickel sulfamate bath was subjected to pre-electrolysis to remove impurity ions like copper, zinc, iron, etc. A nickel anode (20 cm x15 cm) was connected to the positive pin of the DC supply and a stainless steel substrate of the same size was taken as the cathode. A current of 3.1 A/dm^2 using a DC power supply (30V, 30A) was passed through the solution for 16 hours to deposit impurity ions. The obtained solution was then filtered and used as required.

The Ni-sulfamate plating bath (~200 mL) containing 20 g of synthesized / naturally available ceramic particles (100 g/L) was taken in a 500 mL glass beaker at room temperature. A pure nickel sheet (25 mm x 120 mm) and a brass substrate of the same dimension were used as anode and cathode respectively. The grease present on the polished brass substrate (25 mm x 37.5 mm) was removed with acetone. The substrates were cleaned in 20% NaOH at 0.0645A/dm^2 and dipped in 10% H_2SO_4 and finally washed with distilled water. The pH of the nickel sulfamate bath was maintained at 4 and the distributive phase powders were dispersed in the nickel sulfamate bath by stirring the contents of the bath on a magnetic stirrer at 600 rpm using a magnetic stirrer for 15 hours. During electrodeposition, the particles were stirred at 600 rpm based on the optimized studies. The schematic of the experimental setup is shown in Fig.3. The codeposition was carried out at 0.23, 0.77, 1.55, 3.1 and 5.4 A dm^{-2} for 20, 6, 3, 1.5 and 0.75 h at room temperature using a DC power supply to maintain a deposit thickness of approximately 40 mm based on Faraday's laws.

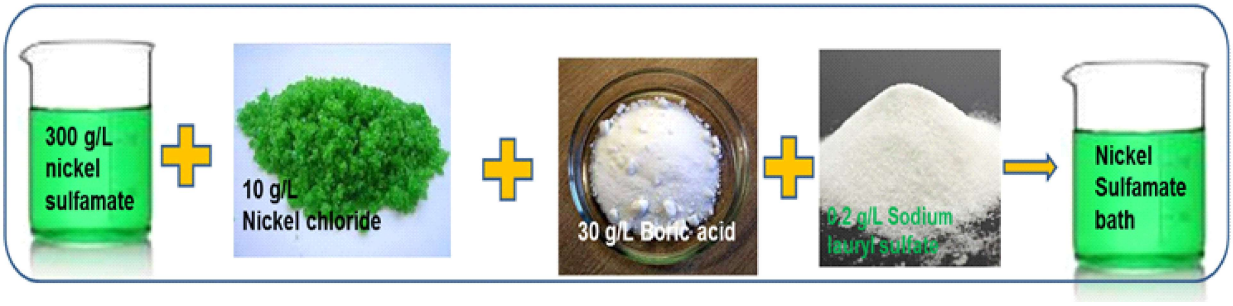


Fig.2. Nickel sulfamate bath preparation steps.

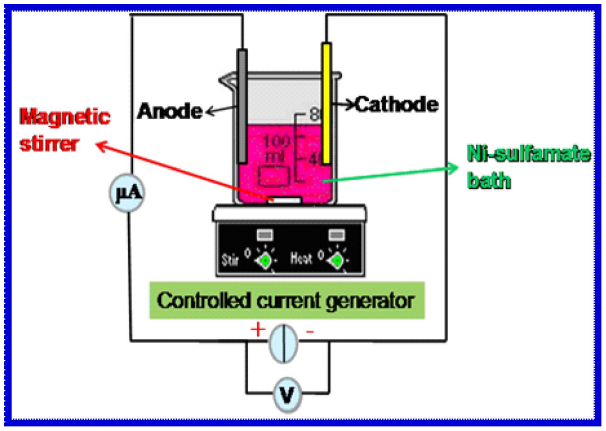


Fig.3. Schematic of the experimental setup used for electrodeposition.

The microstructure, microhardness, wear resistance and corrosion resistance of the developed coatings were characterized using a field emission scanning electron microscope (FESEM), microhardness tester, wear tester and an electrochemical work station. More details regarding the characterization of the coatings are illustrated in the literature [5]. More details regarding the synthesis of oxides by solution combustion method and their use in electrocomposite coating is already reported [6]. The highlights of the Ni-composite coatings developed using various indigenously synthesized or naturally occurring minerals are provided under different sub-headings:

3. Highlights of various Ni electrodeposited composite coatings

3.1. Electrodeposited composite coatings containing synthesized powders

During 2000-2010, in the literature, only commercial ceramic powders were used for the development of electrodeposited composite coatings for enhancing the metal matrix properties. For the first time, the application of solution combustion synthesized ceramic oxides in electrodeposited Ni matrix composite coatings was demonstrated using partially stabilized and fully stabilized zirconia [7]. Thereafter a large number of nanosize oxides like alumina [8], doped alumina [9], different forms of alumina [10, 11], ceria [5], yttria doped ceria [12], titania [13], etc., were prepared. These powders were incorporated in the nickel matrix and improved wear and corrosion resistant properties were obtained for the electrodeposited composite coatings. The systematic studies on Ni-composite coating containing solution combustion synthesized ceria powder provided an easy reference for researchers for researching on electrodeposited Ni-composite coatings [5]. The study clearly showed the influence of applied current density on the area fraction of particles incorporated in the Ni matrix and there was a direct correlation between the area fraction of particles incorporated and the microhardness of the composite coating [5] (Fig.4) . The cross-section of the Ni-CeO_2 coatings showed the uniform distribution of particles (Fig.5).

The Ni/CeO_2 showed improved corrosion resistance (lower icorr value - 0.366 μA/cm^2 compared to 0.6759 μA/cm^2 for Ni) compared to plain Ni. The coatings exhibited adhesive wear as evident from the wear coefficients calculated for Ni/CeO_2 (5.10×10^{-7}) and Ni (3.94×10^{-7}). When ceria was replaced with yttria doped ceria, the corrosion resistance of the Ni-composite coating increased by 1.6 times that of composite coating ceria (Fig.6). This has been attributed to the smaller crystallite sizes of 8YDC, finer Ni crystallites and the effect of yttria [12].

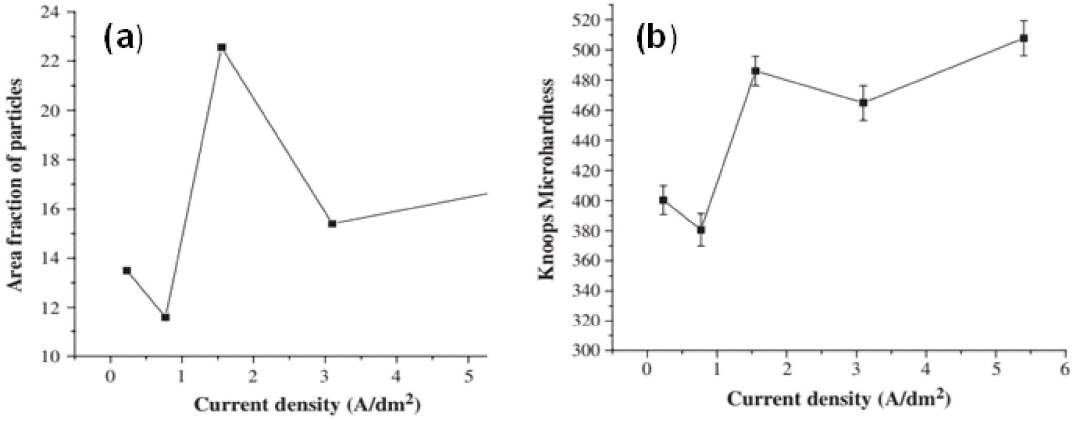


Fig.4. Plots of (a) area fraction of particles incorporated vs. current density and (b) microhardness vs. current density of Ni/CeO_2 [after ref.5].

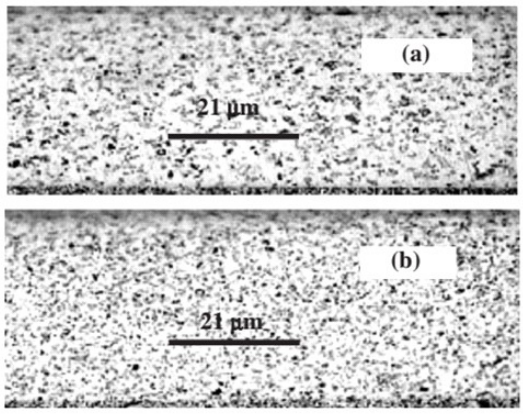


Fig.5. The cross-sectional optical microscope images of Ni/CeO_2 coatings obtained at (a) 0.77 A/dm² for 6 h and (b) 1.55 A/dm² for 3 h [after ref.5].

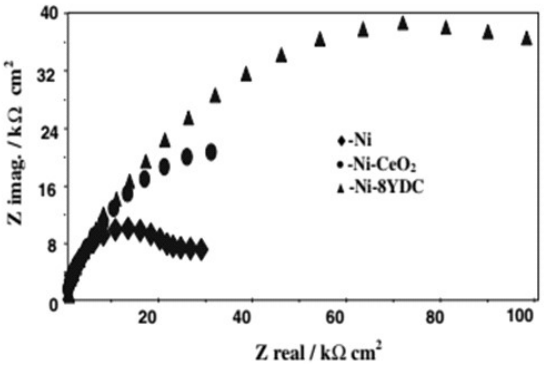


Fig. 6. Nyquist plots of (a) Ni, (b) Ni–CeO_2 and (c) Ni–8YDC Coatings [after ref.12].

In another effort, electrodeposited Ni-zirconia composite coatings containing various mol% of yttria were synthesized [14]. The three powders containing various mol% of yttria doped zirconia were prepared by co-precipitation technique using ammonium bicarbonate as the precipitating agent to obtain YSZ-1(monoclinic), YSZ-2 (tetragonal) and YSZ-3(cubic) zirconia powders. The crystallite sizes of zirconia powders were found to be 19.6, 16.6, and 12.6 nm respectively for YSZ-1, YSZ-2 and YSZ-3 zirconia powders. Among the coatings, Ni-YSZ-2 showed higher microhardness and Ni-YSZ-1 the least. The Ni-YSZ-3 coating showed lower wear loss (0.0415 mm^3). The Ni-YSZ-3 coating showed higher polarization resistance. Thus this study has shown that zirconia powder containing higher mole% of yttria exhibited higher microhardness, wear and corrosion resistance compared to plain Ni and other Ni-YSZ coatings.

During the first decade of 2000, there were only reports on electrodeposited composite coatings containing only simple oxides like alumina, ceria, zirconia and titania as the distributed phases and seldom any composite powders were used to impart synergistic wear and corrosion resistance properties to the Ni composite coating. Cost-effective nanosize yttria stabilized zirconia and alumina (YZA) composite powder and zirconia toughened alumina (ZTA) containing unique combination of alumina and zirconia were prepared by solution combustion method using a mixture of fuels [15]. The developed YZA and ZTA powders were codeposited with

nickel. Interestingly, when YZA was incorporated in the nickel matrix the resulting Ni-composite coating resulted in the synergistic combination of microhardness, corrosion and wear resistance compared to other distributive phases such as ceria, yttria doped ceria and ZTA (Fig. 7). The YZA powder can be synthesized with ease and scaled up; the powder is crystalline in nature does not require any pretreatment or calcination steps and can be used directly in the bath unlike SiC particles and this work was patented [15]. The Ni-YZA coating can find application in the area of reciprocating engine systems, diesel and gas turbine engines, which are subjected to high temperature corrosion and wear. Thus, YZA emerges as a propitious distributive phase for electrodeposited Ni composite coatings.

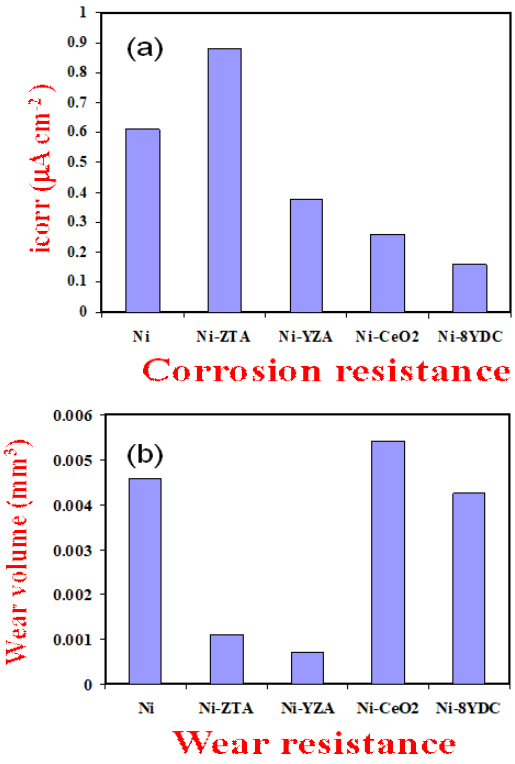


Fig.7. Bar graphs showing the corrosion and wear resistance of electrodeposited composite coatings synthesized in the author's laboratory.

The advantage of using synthesized powders over commercial powders in metal matrix composites to achieve higher microhardness, corrosion and wear resistant properties has been demonstrated by preparing different forms of alumina like α and γ and incorporating them in the Ni matrix [10,11]. Similarly, the co-precipitation synthesized titania powders were tailored such that when they were incorporated into the Ni matrix, the resulting Ni-composite coating exhibits properties similar to that of the Ni-composite coating containing commercial titania powders [13].

For the CSIR supra institutional project on "Composite coatings for trochoid of Wankel engine", a large number of oxide particles were prepared and the properties of the Ni composite coating were evaluated. Among them, nanosize partially stabilized zirconia powder prepared by the mixture of fuels approach when incorporated in Ni matrix had shown great promise. The composite coating has shown higher microhardness and improved wear and corrosion resistance compared to Ni-SiC coatings currently used in trochoid coatings of Wankel engines. The process has been scaled up to prepare 150 g powder/batch.

Tailor-made Al_2O_3–13 wt-%TiO_2 (AT) composite powder that can be used selectively to improve either corrosion or wear resistance or both for the Ni-composite coating were developed [17]. Ni-AT coatings were electrodeposited using physically mixed commercial Al_2O_3 and TiO_2 powders. The corrosion resistance of Ni-AT composite coating was similar to that reported for Ni-TiO_2 and its wear behavior was in between Ni-Al_2O_3 and Ni-TiO_2 coatings.

3.2. Electrodeposited composite coatings containing microcapsules and porous particles as distributive phases

For the first time, the use of porous particles for the development of electrodeposited nickel composite coating was reported [18]. When porous spray dried fine powder was used as the distributed phase in the Ni bath, during co-deposition, in-situ Ni impregnated alumina particles (Fig. 8) were electrodeposited and the resulting Ni-alumina coating exhibited microhardness (654 HK) higher than the coating containing commercial alumina powder (500 HK). This study has shown that porous particles can be exploited in the development of metal matrix composites as the distributed phase with improved

adhesion of the particles along with higher microhardness and wear resistance.

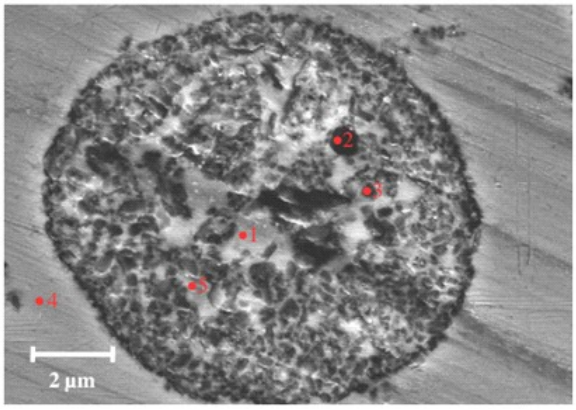


Fig.8. Scanning electron microscope image of the cross-section of electrodeposited Ni–porous alumina particles (red spots correspond to nickel) [after ref.18].

Oil filled microcapsules are propitious candidate materials for developing electrocomposite coatings exhibiting outstanding tribological properties [19]. Lubricating oil containing microcapsules were successfully synthesized using in-situ interfacial polymerization method and incorporated into the nickel matrix (Fig. 9). Some of the challenges in codepositing the oil containing microcapsules were overcome by adapting a simple washing procedure for the microcapsules. The chosen method for synthesizing microcapsules was simpler and cost-effective and yielded rigid microcapsules which retained their shape in the composite coating. The developed Ni-microcapsule composite coatings were found to exhibit improved tribological properties with lower wear loss and lower coefficient of friction (0.2) compared to plain Ni coating (>0.4) (Table-1).

3.3. Electrodeposited composite coatings containing natural minerals and fly ash waste

In the pursuit of developing cost-effective electrodeposited composite coatings, pumice stone, a volcanic rock powder was used as the distributed phase [20, 21]. The developed coating has shown

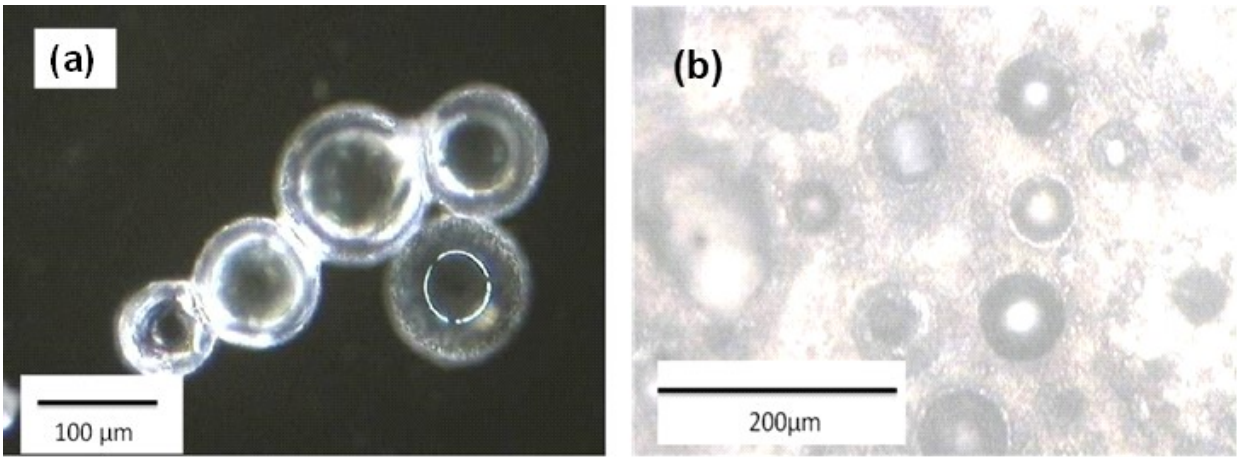


Fig.9. Optical microscope images of (a) oil-filled microcapsules and (b) surface image of Ni-microcapsule composite coating.

Table 1. Comparative wear properties of Nickel and Nickel-microcapsule coatings.

Sample	Wear loss (ìm)	Hardness (HK)50gf	Wear volume loss (mm^3)	Wear coefficient	Wear rate	Coefficient of friction average
Ni	75	290	0.08787	$1.12x10^{-5}$	$3.88x10^{-5}$	0.40
Ni-microcapsule	18	390	0.003045	$7.88x10^{-7}$	$2.02x10^{-6}$	0.20

improved microhardness, wear and oxidation resistance that was equivalent to the conventional Ni-SiC coating (Fig. 10). The pumice particles are 15 times cheaper than SiC particles. This coating is very promising for industrial applications.

Zircon a naturally available mineral that is cost-effective compared to the oxides and SiC powders was explored as a new distributive phase for the development of Ni metal matrix coatings [22]. The effect of surfactants on the properties of the coating was also studied. The study has clearly shown that naturally occurring zircon and Cetyl Trimethyl Ammonium Bromide (CTAB) to be a propitious distributive phase and surfactant respectively. CTAB addition resulted in the incorporation of a large number of smaller particles. The use of sodium hexametaphosphate as a new surfactant for improving particle incorporation and in turn the microhardness of Ni-SiC system has been demonstrated [23].

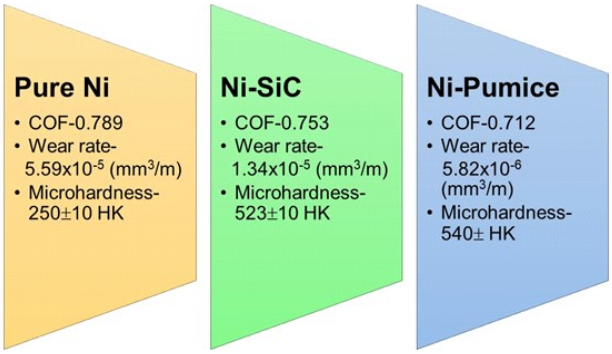


Fig. 10. Comparison of the microhardness and tribological properties of electrodeposited Ni, Ni-SiC and Ni-pumice coatings.

The application of fly-ash cenospheres as the distributed phase in the electrodeposited Ni composite coating was explored for wear resistant applications [24]. The study showed that when the particle loading was 125 g/L, the obtained coating exhibited a lower coefficient of friction. (Fig. 11) Further, detailed studies are required to understand the mechanism. Electrodeposited Ni-cenosphere coatings are cost-effective as cenospheres are a byproduct of fly ash and industries can adapt this easily.

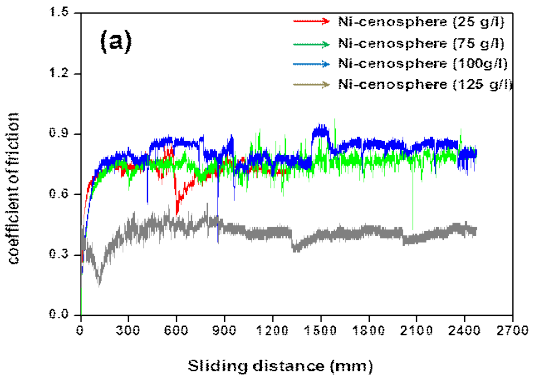


Fig.11. Plot of coefficient of friction vs. sliding distance for electrodeposited Ni-cenosphere composite coatings containing different amounts of particle loading.

Conclusions

Electrodeposited Ni-composite coatings containing oxide particles can replace the Ni-SiC coating. In this pursuit, significant work has been carried out at CSIR-NAL to replace SiC with synthesized simple and complex oxides, naturally occurring minerals, industrial waste, oil-filled microcapsules, etc. Yttria doped zirconia-alumina composite powder is a propitious oxide powder that imparts synergistic wear and corrosion resistance to the electrodeposited composite coating. Pumice emerged as a successful candidate to replace the expensive SiC powder as the distributed phase in the electrodeposited Ni composite coating. Effort towards the synthesis of Ni composite coating containing oil-filled microcapsules was successful. The cenospheres, a byproduct of fly ash can also be utilized to improve the wear resistance of electrodeposited Ni composite coatings. It can be summarized that the author's group screened naturally available minerals and industrial waste materials and synthesized simple and composite oxide materials and that can be used as distributive phases in-lieu of SiC in electrodeposited Ni-composite coatings that are promising cost-effective coatings which can find industrial applications.

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