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“TRIBOLOGICAL BEHAVIOUR OF NICKEL-SILICON NITRIDE CO-DEPOSITED COMPOSITE COATINGS”

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ABSTRACT

Dispersability of nano ceramic particles into the electrolytic bath has always been an issue of debacle in the published literature. Without proper dispersion of the nanoparticles into the electrolytic bath, electrodeposition could not be carried out. Upon decreasing the alkalinity of the suspension, nanoparticles tend to agglomerate at a faster rate. This present thesis deals with surface properties of coatings embedded with composite materials at various composition. The dispersion of silicon nitride nanoparticles (particle size < 100nm) into the Watt's nickel bath and thus leading to the electrodeposition of Ni-Si₃N₄ nanocomposite coatings. Electrodeposition of Ni-Silicon nitride nanocomposite is performed. Surface characterization through scanning electron microscopy (SEM) and Vickers hardness test are performed to analyze silicon nitride composite coating done from various electrolytic bath compositions prepared to test the agglomeration of the particles.

Key Words: Dispersion, Nanoparticles, Scanning electron microscopy, Suspension, Agglomeration, Coating.

I. INTRODUCTION

Nano-structured Materials

Nanostructured content signify the type of components that are organized as single or multi-phase crystalline shades with a feed dimension few nanometers, generally less than 100 nm. As a result, nano-crystalline content display the qualities that are considerably enhanced over their traditional rough grained polycrystalline counterparts [1]. Nano-crystalline components can be categorized into different groups depending on the variety of measurements in which content has nanometer inflection, such as (a) one dimensional, padded or lamellar framework, (b) two dimensional, rod-shaped framework and (c) three dimensional, equi-axed nano-materials. However, the equi-axed is mainly the most common of all groups having all the three nanometer scaled measurements and is known as as nano-structured crystallites and nanoclusters. As far as features of nano-materials are involved, in a wide variety, it is depending on top-down and bottom-up techniques. The former appears for the splitting down of the large content into smaller sized measurements whereas the later is depending on combining the small groups. Top-down strategy causes some natural disadvantages like flaw of surface framework and important crystallographic harm to the prepared patterns [2]. While the bottom-up strategy usually depending on substance ways of production is versatile in its use and performs an important role in the fabrication and processing of nanostructures. To apprehend the phenomenon of grain size dependent strength of nano-crystalline material a lot of work has been done. A lot of work has been done to accommodate grain size dependence of strength of the nano-crystalline materials.

In the area of content technology, significant improvements have been made for the features of nanostructured components with enhanced technical, substance and tribological properties. A huge variety of techniques have been researched and applied to synthesize nanostructured components among which are inert gas condensation, technical alloying, electrodeposition [3-7], rapid solidification from the melt physical vapour deposition, chemical vapour deposition, sol-gel processing, sliding wear, spark erosion, plasma processing, laser ablation, quenching the melt under high pressure, templating, and the devitrification of the amorphous phases.

A huge variety of research has revealed that one could change the qualities of nano-crystalline components through the management of micro-structural features, more particularly the grain size. It is generally noticed that the durability of polycrystalline content improves with the loss of grain size known as as Hall-Petch relation, however an inverse Hall-Petch impact for nano-crystalline components has been exposed by many authors [8, 9]. The results suggest that nano-crystalline components get softer as grain size is decreased below a critical value which is presumed to differ for different components. The heap up of dislocations at grain boundaries is a key procedure of Hall-Petch relationship. But this relation ceases to exist when grain size fall below the stability range between the dislocations. However, the difference from Hall-Petch relation can obviously be linked to a difference from dislocation taken over deformation and grain boundary sliding control process. Some of the scientists are of the perspective that yield strength of material is both reliant on stress rate and heat range, and that it varies from the Hall-Petch relationship as the vital grain size [8].

Nano-crystalline alloys

In order to improve the performance of existing materials, quite a number of nano-crystalline components have been developed recently. For this purpose, a wide range of new and non-equilibrium (meta constant state) handling methods such as rapid cooling from the liquid stage, moisture build-up or condensation from the vapour baths or electrodeposition from the electrolytic baths etc. followed by heat treatment of the amorphous precursor, have been progressed for the features of nano-structured single stage, binary stage or ternary stage elements. Moreover, thermal devitrification of the components prepared by above mentioned methods have also been employed to obtain nano-crystalline components with uniform grain size. Due to extremely fine grain size, nano-crystalline components both bulk and coatings display a wide range of qualities that are different and at times mostly enhanced when compared to traditional rough grained polycrystalline components. These include morphological or architectural qualities, improved strength or firmness, enhanced diffusivity, enhanced ductility, strength or flexible modulus, lower heat conductivity, improved deterioration or wear [10]. Moreover, due to small dimension and grain boundary area, nanocrystalline components display solubility towards solute atoms. In this way unique qualities appear that are culminations of novel nanostructures and enhanced compositional effects.

Electrodeposition

Electrodeposition is simple and economical technique for the dense metallic nanocrystals [29]. DC, PC and PRC electrodeposition methods are used to fabricate metallic coatings. Qu et al deposited nickel coatings by DC and PC electrodeposition method and observed significant improvement in hardness in PC electrodeposited coatings than DC electrodeposited nickel coatings [27]. Tao et al fabricated nanocrystalline copper coatings to study the tribological and mechanical properties of the copper coatings [30]. Copper coatings deposited by PC electrodeposition technique have higher hardness and wear resistance compared to DC electrodeposited coatings. Pure nickel coatings deposited by PC and PRC techniques have better corrosion resistance than DC electrodeposited nickel coatings. This chapter provides a brief overview on DC, PC and PRC electrodeposition methods.

Electrodeposition presents a cost effective and less equipment intensive method for the preparation of nanocrystalline and nano phase metallic particles (metals, alloys, compositionally modulated alloys, composites) either in the form of coating or freestanding objects even of complex shapes like foils or wires. The low processing temperature tends to minimize inter diffusion or chemical reaction. The film thickness can be controlled by monitoring the consumed charge. The potential of electroplating, especially for nanomaterials processing has been appreciated in terms of highly dense structure, no post treatment, ease of formation of bulk nanostructures for a wide range of material systems with a high production rate.

II. LITERATURE SURVEY

Co-deposition of nickel composite coatings

Nickel composite coatings usually deposited from Watts type or sulfamate bath containing nanoparticles (i.e. SiC ,
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Al_2O_3 , ZrO_2 , TiO_2 , WC , SiO_2 , and CNTs) are in suspension. The improvement in hardness is due to the combination of both rule of mixture and dislocation pinning effect [23]. Additions of nanoparticles mainly inhibit grain growth and promote nucleation sites.

Properties of nickel composite coatings

Mechanical properties of nanocrystalline components mainly rely on microstructure of material enabled dislocation concept correlating with strength and ductility of these materials. Nickel composite coatings involve nickel matrix containing distribution of second stage composites, such as Al_2O_3 , Si_3N_4 , SiC , Cr_2O_3 , WC , diamond, PTFE, graphite, or even fluid containing microcapsules to enhance mechanical, tribological, and corrosion resistance properties of nanocomposites. These second stage composites act as physical hurdle to dislocation activity and grain boundary movement causing into significant enhancement in mechanical qualities of blend coverings.

Hardness

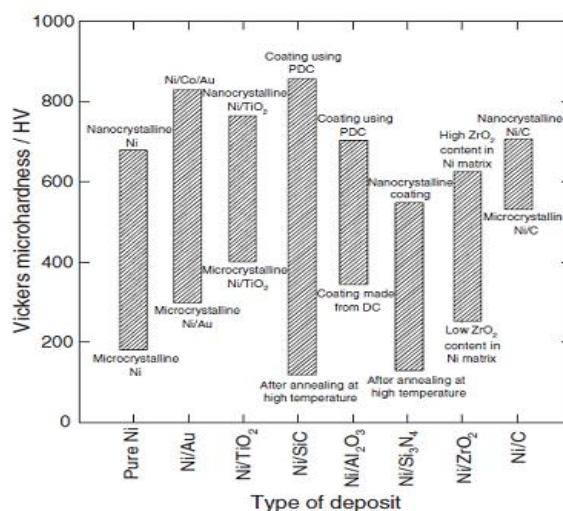


Fig. 1 Vickers hardness values for different range of particle size in nickel deposit. [2]

Stiffness of material is identified as the level of resistance of a material to deformation particularly permanent deformation, indent or scratching. Generally, hardness is related to the tensile yield stress due to geometric restriction caused by deformation by

$$H = 3\sigma_y$$

Addition of ceramics to synthesize blend coverings act as a hurdle to dislocation activity and grain boundary movement thus increasing hardness of the composite coatings. Increase in hardness of blend coverings is due to the mixed impact of grain enhancement due to Hall-Petch method and consistent distribution of nano-particles due to Orowan technique. Therefore, impact of strengthened contaminants in blend coatings on hardness relies upon mainly on amount of material as well as size and submission of these contaminants in the nickel matrix [28]. Firmness of blend coverings is mainly influenced by two aspects:

- Firmness of nickel matrix which is identified by microstructure of the coatings.
- Volume material of strengthened ceramic particles in the composite coating.

Evaluation of Vicker's microhardness for a variety of nickel composite coatings is shown in figure.1. It clearly reveals significant enhancement in hardness of blend coatings in comparison to genuine nickel coatings.

Corrosion resistance

Nickel composite coatings have better level of corrosion resistance than genuine nickel coverings because strengthened second stage contaminants affect the regular development of nickel amazingly and promote new nucleation site. This makes framework of blend coverings more perfectly crystalline and hence enhanced corrosion resistance of blend coverings [29, 30]. Addition of these contaminants in blend coverings will reduce deterioration present solidity and will move deterioration potential of blend coverings towards more noble direction. Vickers microhardness principles for different ranges of compound size in nickel deposit. These are proven from lowest to highest possible (bottom to top) found in the literature. Amadeh et al conducted electrochemical tests to evaluate corrosion actions of (Ni-SiC) composite

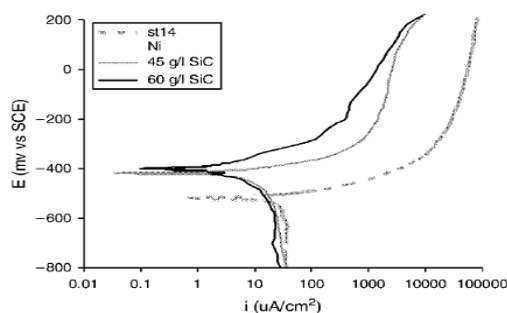


Fig. 2 Polarization curves of st14 steel, pure nickel and composite coatings: produced at the current density of 4 A/dm², duty cycle = 30%, frequency 10Hz from baths containing 45g/L and 60g/L SiC [3]

Figure 2 clearly reveals corrosion resistance of composite coatings has significantly enhanced in comparison to genuine nickel coverings and stainless-steel substrate [10]. Almost all nickel composite coatings strengthened with Al₂O₃, SiC, TiO₂, CNTs, Si₃N₄, and WC show better corrosion resistance when compared to genuine nickel coatings.

Watt's nickel bath

Watt's nickel bath is capable of depositing both bright and semi-bright nickel. Bright nickel is used for decorative purposes while semi-bright is used for engineering applications. The bath consists of Nickel sulphate hexahydrate (NiSO₄.6H₂O), Nickel chloride hexahydrate (NiCl₂.6H₂O) and boric acid (H₃BO₃). Table 1 shows the composition of chemicals required to prepare 1L of Watt's nickel bath:

Table 1 Composition of Watt's nickel bath

CHEMICAL	CONCENTRATION
NiSO ₄ .6H ₂ O	375 – 400 g/L
NiCl ₂ .6H ₂ O	40 – 60 g/L
H ₃ BO ₃	30 – 50 g/L

Boric acid is added as it acts as a buffer to Watt's bath and maintains the pH value in the cathode solution interface. It also acts as a catalyst which lowers the overvoltage for nickel deposition. Hydrochloric acid (HCl) or Sodium hydroxide (NaOH) is added to solution to adjust the pH to 2.5.

Electrodeposition set up

Generally, during electrodeposition of metal or cermet coatings over the surface of the cathode the set up used is vertical (conventional electro co-deposition) i.e. surface on which deposition needs to take place is at the right angles from the bottom surface of the beaker.

Electrochemical cell

To carry out the electrodeposition of the metal or metal matrix composites over the base surface an electrochemical cell is required. An electrochemical cell comprises of following components:

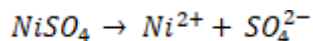
- Electrolytic solution
- Cathode (as substrate-EN8 used in present thesis)
- Anode (stainless steel used in this thesis)
- Direct current / pulse current generator

Other components required to provide better coating surface and speed up the reaction inside the cell:

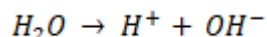
- Mechanical agitator
- Hot plate to raise the temperature of the electrolytic bath

Mechanical agitator is used to maintain the homogeneous dispersion of the ceramic particles inside the electrolytic bath and temperature acts as a catalyst to speed up the decomposition reaction.

For the present electrochemical cell, Watt's nickel bath is used with dispersed silicon nitride nanoparticles. Upon applying the electric field in the electrolytic solution using DC or PC generator, nickel sulphate dissociates the following way



While the water dissociates into



This decomposition of nickel, due to application of the electric field helps in the deposition of the nickel over the surface of the cathode. Nickel forms a matrix over the cathodic surface and silicon nitride nanoparticles are entrapped into these matrices. This phenomenon in an electrochemical cell provides thick, uniform cermet coatings over the surface of the substrate.

III. RESULTS & DISCUSSION

Surface morphology of electrodeposited Ni-Si₃N₄ composite coating

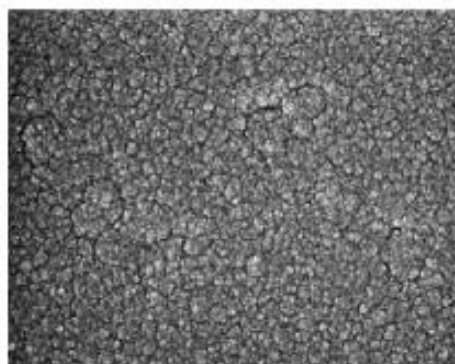
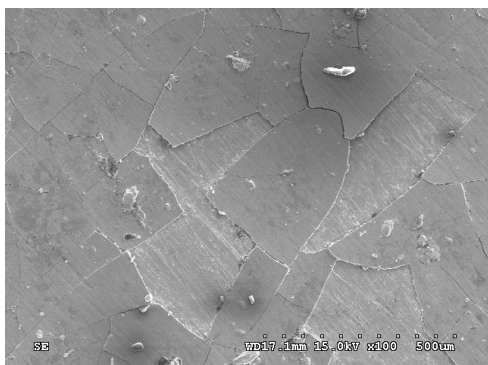


Fig. 3 SEM image of pure Nickel coating **Fig. 4** SEM image of 2% Silicon Nitride composite coating

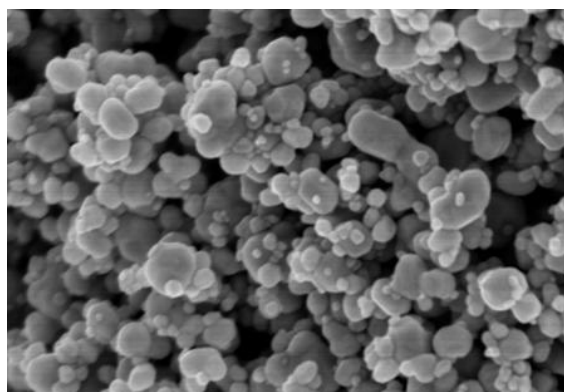
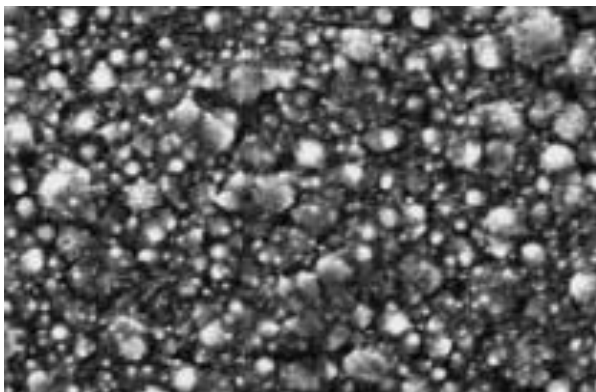


Fig. 5 SEM image of 4% Silicon Nitride composite coating Fig. 6 SEM image of 6% Silicon Nitride composite coating

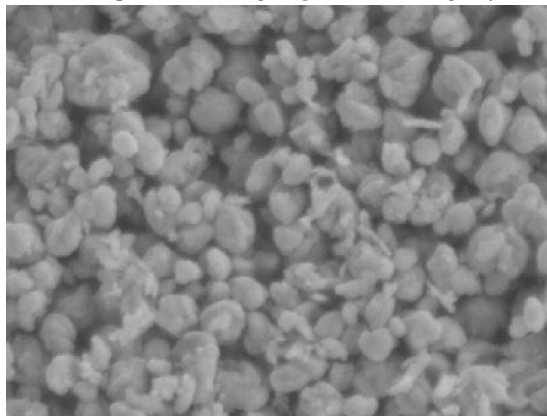


Fig. 7 SEM image of 8% Silicon Nitride composite coating

The nanocomposite coating of Nickel-Silicon nitride is deposited through direct current electrodeposition. Images of nanocomposite coating through scanning electron microscope are taken. Uniform grain size spread throughout the composite coating are observed as depicted in fig. 4.5 and 4.6. Various magnifications of the images are kept like 100x, 200x, 1000x, 2500x and 5000x to closely analyse the presence of silicon nitride nanoparticles in the composite coating. At lower magnifications, nanosized particles could be observed at distant locations. It could be interpreted from the images that the distribution of silicon nitride ceramic particles in the nickel matrix is not uniform and thus homogeneous coating is not obtained.

Microhardness of Nanocomposite coatings

In the present thesis, samples of EN8 are coated with nickel and nickel-silicon nitride nanocomposites. The weight percentage of silicon nitride in the coating is 0.1 and 1%. These coatings are subjected to the microhardness test. Test was done so as to ascertain the increasing value of hardness in of the surface of the coating as the percentage of silicon nitride ceramic particles increase in it.

The values of hardness showed positive results at the composition of 1% silicon nitride particles by weight. Six hardness values are calculated for each sample using formula for Vicker's hardness:

$$HV = \frac{0.1854 F}{d^2}$$

Where:

F = Test load (N)

D = Average diagonal length of an indentation (mm)

If the test load is in Kgf then,

$$HV = \frac{0.1854 F}{S}$$

Where:

S = Surface area of an indentation (mm²)

It is evident from the figure that as the weight% of ceramic particle in the coating increases the hardness increases to a considerable value.

For every sample each of 6 observations were taken to calculate the value of Vicker's hardness. Several values are taken to consider every location on the substrate's surface and thus reach a mean value which can be quoted as the hardness of the coating at a particular value of silicon nitride particles incorporated in it.

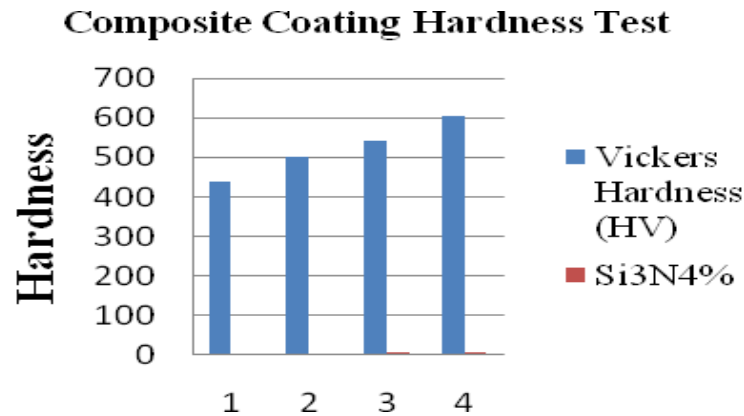


Fig. 4.6 Bar Graph plot depicting hardness at various level of silicon nitride incorporation in nickel

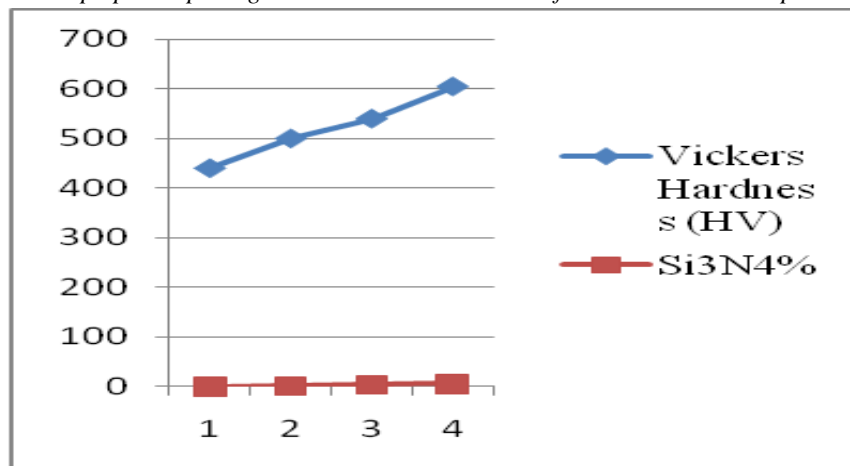


Fig. 4.7 Hardness at various level of silicon nitride incorporation in nickel

IV. CONCLUSION

The Electrodeposition of Ni-Si₃N₄ nanocomposite is carried out in Watt's electrolytic bath. Electrodeposition of nanoparticles is a challenging issue due to instability of silicon nitride nanoparticles in the Watt's electrolytic bath.

SEM results confirmed the incorporation of Si₃N₄ nanoparticles in the coating in the nanocomposite bath used for co-deposition. Satisfactory level of incorporation of the particles in the coating is observed.

Also, Vicker's hardness values for the coating are calculated at 100gm loads with silicon nitride weight% 2%, 4%, 6% and 8% in the composite coatings. With respect to nickel coatings, tests revealed satisfactory results by increasing hardness at incorporation level though difference in hardness as incorporation increased.

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