

Effect of Addition of TiO_2 Macro Particles on Electrodeposited Ni-B Coatings

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Abstract

This study focuses on understanding the effect of TiO_2 micro particle introduction on surface morphology, structure, thermal stability, mechanical properties, and corrosion performance of NiB coatings. The surface morphology is observed to become rough and irregular by the addition of the TiO_2 micro particles. However, TiO_2 micro particle inserted NiO coating (NiB-TiO_2) retained the clusters of grains type morphology as that of NiB coating. The crystallinity of NiB coating increased by addition of TiO_2 particles and no significant changes in the thermal behavior of the NiB coating is observed by the formation of NiB-TiO_2 composite. Upon addition of TiO_2 the mechanical properties NiB composite such as nano hardness and elastic modulus and corrosion potential improved. The improvement in hardness, elastic modulus was clearly due to addition of the harder and stiffer TiO_2 particles which caused Orowan strengthening while the improved corrosion performance was attributed to the reduction in significant number of active corrosion sites brought about by the introduction of inert TiO_2 particles.

Keywords: Nano composite; Coating; Electro deposition; Ni-B; Ni-B- TiO_2

Introduction

Nanocrystalline materials have been fascinating, as they fill the gap between conventional coarse grained and amorphous materials. Since their invention three decades ago, a lot of effort has been directed to understand and to develop further the properties of nanocrystalline materials [1]. These exotic materials have been found to bear properties superior to their conventional counterparts, except for poor thermal stability and limited ductility [2]. For a long time, the production of fully dense, defect free nanocrystalline materials as necessary for widespread applications was a challenge. Although powders with a nanocrystalline structure produced by mechanical milling or inert gas condensation routes could be compacted by methods such as hot isostatic pressing, shock consolidation, etc. without bringing a significant change in their nanocrystalline nature, the achieved density was found to be lower than that required for structural applications [3]. Furthermore, the achievement of full density with increasing processing temperature was limited by the grain growth tendencies demonstrated by these concerned materials [4]. Hence, the bulk production of nanocrystalline materials using the two steps process is still a work in progress, although recent developments with thermally stable nanocrystalline materials and field activated sintering techniques are encouraging [5,6].

In contrast to the two steps process, the production of near theoretical dense nano crystalline materials *via* one step processes such as severe plastic deformation, electrodeposition, etc. have found greater success from the viewpoint of ease of processing of complicated shapes and/or bulk parts and the suitability of the products for the real world applications [7,8]. Consequently, nanocrystalline materials produced by these techniques, especially those by electrodeposition are under consideration for

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commercial applications. For example, coatings based on nanocrystalline nickel and its alloys are being actively considered as a replacement for the environmentally detrimental hard chrome plating [9-12]. Schuh and co workers have demonstrated nanocrystalline coatings of Ni-W alloys as a suitable alternative for hard chrome plating. Similarly, other possible alloys of Ni such as NiB, NiP have been developed as alternatives to the hard chrome plating [13-15]. The key performance indicators of these coatings are strength, wear resistance and corrosion resistance. Although nanocrystalline coatings of elemental Ni provide satisfactory corrosion resistance, they fall short on strength and wear resistance and this necessitates the development of nanocrystalline nickel based composites. Because of many advantageous properties such as hardness, wear resistance and corrosion resistance, etc. NiB composite coatings are considered suitable for many industries viz petrochemical, printing, electronic, aerospace and automotive [16-24]. The properties of composite NiB coatings can be further improved by addition of other elements or compounds. Additions of such elements or compounds have improved the mechanical properties and chemical resistance of the coatings. There is space for the improvement, investigation and exploration of the addition of elements or compounds which can further help to enhance the properties of the composite like wear resistance, corrosion, hardness, etc. [25-30].

In this study, mechanical properties, as well as corrosion behaviour of nanocrystalline NiB and NiB-TiO₂ composites are evaluated. The choice of TiO₂ as the reinforcement particle is guided by the fact that it is a ceramic and hence is expected to provide strength to the matrix. Besides, it has anti-fouling and photochemical properties and thus may provide added functionality to the coating.

Materials and Methods

NiB and NiB-TiO₂ composite coatings were deposited by electrolytic technique on steel substrates having dimensions of 22 mm × 2 mm using direct current from an aqueous solution. Pristine nickel plate and low carbon steel were employed as anode and cathode respectively. Before deposition, all samples used were polished by various grades of emery paper (80, 500, 800, 1000, 1200, 2500, 4000) to remove the contaminants present on its surface and to get a flat mirror like smooth finish. After polishing with different grade size emery paper, substrate was degreased using acetone, followed by cleaning with alkaline solution and rinsed with deionised water. After this the substrate was activated with 20% HCl solution for 1 minute and the washed thoroughly with deionised water. Electrolyte composition, parameters employed for electrodeposition of NiB and NiB-TiO₂ on substrate is given in Table 1.

TABLE 1. Showing electrolytic composition, deposition parameters.

Substrate conditions	Quantity g/L	Working
NiSO ₄ .6H ₂ O	240	4.0-4.5 (pH)
NaCl.6H ₂ O	45	55 ± 2°C (BT)
H ₃ BO ₃	30	30 min (Deposition time)
DMAB	3	50 mA/cm ² (Current)
TiO ₂ no particles	0-15	600 rpm
BT: Bath Temperature.		

The electrodeposition was carried out at 55 ± 1°C for 30 minutes. Vigorous agitation of the electrolyte was maintained during the coating process to get uniform covered surface and to prevent precipitation of TiO₂ particles. The NiB-TiO₂ coatings were prepared by adding TiO₂ particles into the electrolyte solution of similar composition from which Ni-B coating has been deposited. Thermo, iCAP 6500, USA made ICP-AES (Inductively coupled plasma atomic emission spectroscopy), EDX (Energy dispersive spectroscopy) technique was used to determine the chemical composition of the coatings. XRD (X-Ray Diffraction) was used to get information about different phases and to determine the structure of the synthesized coatings by using Cu-Kα radiation. The thermal stability of the coatings was studied using a Perkin-Elmer make “Differential Scanning Calorimetry” (DSC). The scans were recorded from 25°C (rt)-450°C in an inert argon atmosphere. The nanomechanical properties *i.e.* hardness and elastic modulus of NiB and NiB-TiO₂ coatings were determined by using MFP-3D nano-indenter attached with a standard tip indenter (spring constant equals 4000 Nm⁻¹). The Berkovich diamond indenter tip consisted of an industrial diamond that was brazed to a screw threaded hex tooled metallic chuck. The indentation measurement was done by using 1 N/m unit indentation force. The contact depth was calculated by unloading curve using Oliver and Pharr method. The nanomechanical properties were analysed from five different zones of two different samples in each case. Corrosion resistance of the coatings

were investigated using potentiodynamic linear polarization technique. The polarization scans were recorded at room temperature in 3.5 weight% sodium chloride aq. solution using three electrode system. The potentiodynamic tests were conducted twice on two different samples in each case to confirm their reproducibility.

Results

Compositional analysis

The elemental identification was carried out using the ICP-OES instrument. Table 2 shows the results of the compositional analysis in weight (%). From the table it is evident that NiB-TiO₂ contains 12.80 weights (%) of TiO₂.

TABLE 2. Showing the analysis of NiB and NiB@TiO₂ composite coatings in weight (%).

Sample	Ni	B	TiO ₂
NiB	84.12	15.88	-
NiB-TiO ₂	73.80	13.39	12.80

Surface morphology

The surface of NiB coating is seen almost uniform, smooth and consists of globular clusters of grains (Figure 1 (a)). It is found to be free from any macroscopic defects such as voids or pores and thus indicates a dense coating. Whereas the NiB-TiO₂ coating is rough and irregular as shown in Figure 1 (b). However, it also bears globular clusters of grain type morphology as that of NiB coating with visible embedded particles of TiO₂. The globular clusters as a case of the NiB-TiO₂ coating are more defined and protruding on the surface. Despite higher irregularity, no defects are observed on the surface of the NiB-TiO₂ coating. This indicates the formation of a dense coating even after the addition of micron size TiO₂ particles.

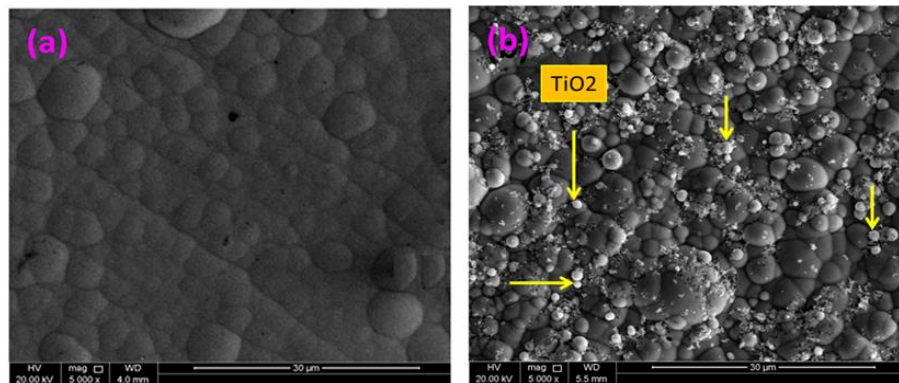


FIG. 1. SEM image of (a) NiB; (b) NiB-TiO₂ composite coatings.

XRD analysis

Figure 2 comparatively shows the XRD curves of NiB, NiB-TiO₂ coatings, pink trace corresponds to NiB and blue trace shows XRD curves of NiB-TiO₂ coatings. XRD curve of NiB consists of a single broad peak whereas that of NiB-TiO₂ coating is observed as sharp crystalline peaks. The broad peak in case of the NiB peak signifies its amorphous nature. The XRD peaks of NiB-TiO₂ all correspond to those of pure nickel.

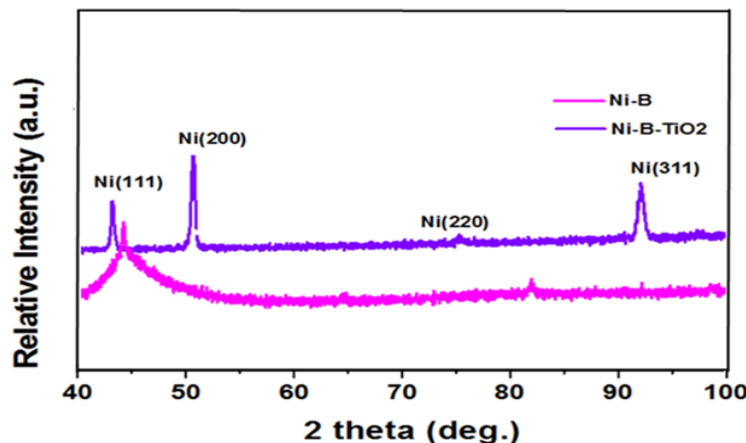


FIG. 2. Comparison of XRD spectra of NiB and NiB-TiO₂ composite coatings.

The (111) XRD peak of NiB-TiO₂ coating is shifted to the left of (111) peak of NiB coating, which is situated almost at the standard position. This indicates a decrease in inter planar spacing of the nickel matrix in case of NiB-TiO₂ coating. It can be concluded from this observation that the addition of TiO₂ micro particles into the NiB matrix leads to the development of compressive stress in the coating. It can also be seen from the XRD graph that introduction of TiO₂ micro particles in the NiB matrix not only increases crystallinity but also leads to texturing. However, no peaks with respect to the presence of TiO₂ particles are observed.

Thermal stability

DSC studies were carried out on the NiB and NiB-TiO₂ coatings from room temperature to 450°C to understand the thermal stability of the coatings. Figure 3 illustrates, both the coatings despite their differences in microstructure displayed an exothermic peak around a temperature of 375°C. The peak is at lower temperature in case of NiB-TiO₂ coating (371°C) and is observed to be more prominent in case of NiB coating. The heat flow in the NiB-TiO₂ coating after approximately 250°C decreases rapidly in comparison to the NiB coating with increasing temperature. This indicates a faster decrease in heat capacity of NiB-TiO₂ coating beyond 250°C in comparison to NiB coating. In case of steel substrate, drop in heat flow is observed even more. However, the depth of the peak observed in the case of NiB coating is more than that observed in case of the NiB-TiO₂ coating.

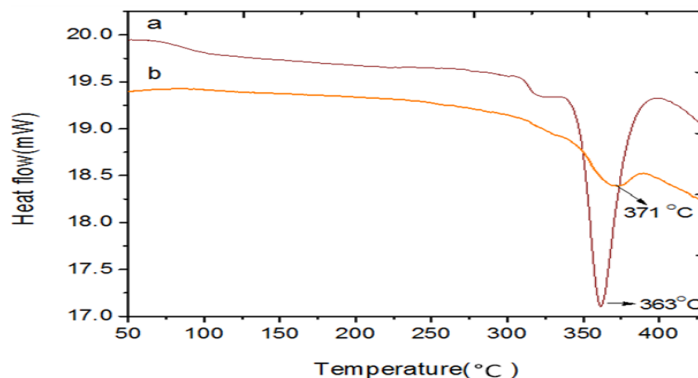


FIG. 3. Comparison of DSC scans (a) NiB; (b) NiB-TiO₂ composite coatings.

Hardness

Elastic modulus and hardness of the substrate, NiB coating and NiB-TiO₂ coating, as determined from the nanoindentation tests are shown in Figure 4 (a) and (b), respectively. The hardness and the elastic modulus of the NiB-TiO₂ coating are observed as approximately 40% and 20% higher than that of NiB coating, respectively.

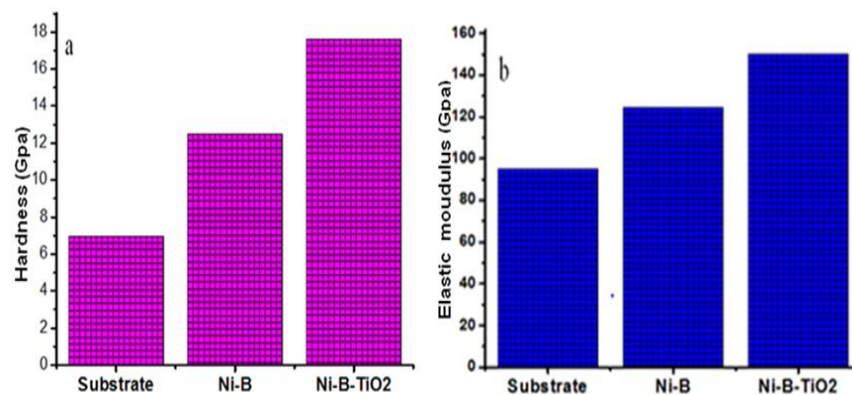


FIG. 4. Showing nanomechanical properties of the steel substrate, NiB, and NiB-TiO₂ composite coatings.

Figure 5 comparatively shows the hardness of NiB and NiB-TiO₂ coatings prepared in the current work with some other nickel matrix composite coatings prepared by other researchers. The results indicate that the NiB-TiO₂ coating exhibits similar or higher hardness than most of the composite coatings reported in the literature. It is almost thrice as hard as the nanocrystalline nickel and almost twice as hard as the hard chrome coating.

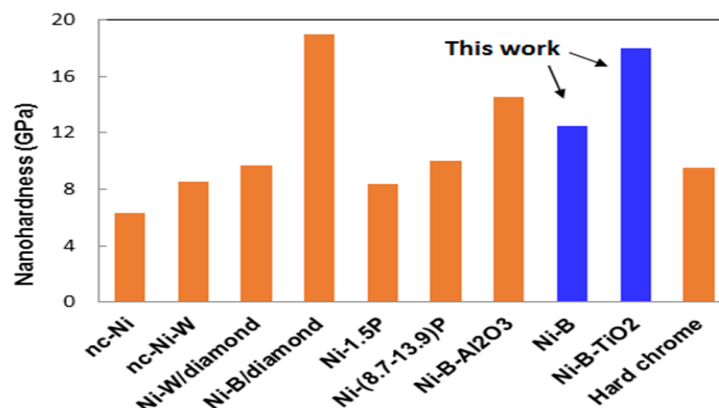


FIG. 5. Comparison of the nano hardness of the coatings produced in this work to that reported in the literature.

Aqueous corrosion resistance

The corrosion behaviour of coatings, as evaluated from the potentiodynamic Tafel plots revealed higher corrosion resistance of NiB-TiO₂ coatings *vis-a-vis* the NiB coatings (Figure 6). It can be observed from the figure that the NiB-TiO₂ coating is nobler as compared to NiB coating since it exhibits less corrosion current and more corrosion potential. Quantitatively, the corrosion current, corrosion potential exhibited by NiB-TiO₂ coating are 29% lower and 19% higher than that of NiB coating, respectively. Both the coatings demonstrate a better corrosion performance as compared to the substrate steel. The quantitative values of potentiodynamic polarization studies are summarized in Table 3.

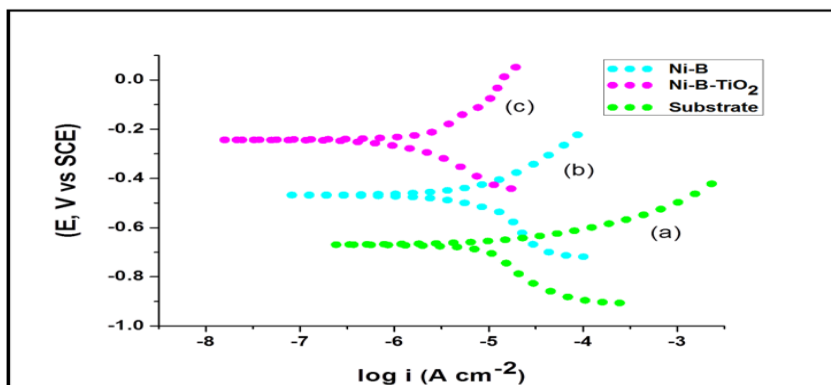


FIG. 6. Potentiodynamic linear polarization curves of (a) steel substrate; (b) Ni-B; (c) Ni-B-TiO₂ composite coatings in 3.5 % NaCl aqueous solution.

TABLE 3. Tabulated below is the corrosion value of steel, NiB and NiB-TiO₂ composite coatings materials.

Sample	E _{corr} (mV)	I _{corr} (μA)	β _a mVdec	β _c mVdec	η (Protection) %
Substrate	-(624.0)	+(21.50)	+(70.0)	+(584.7)	~
NiB	-(504.0)	+(16.80)	+(336.5)	+(465.5)	+(27)
NiB-TiO ₂	-(600.0)	+(11.90)	+(79.30)	+(215.2)	+(90)

Discussion

Compositional analysis

The incorporation of the boron into the nickel matrix is due to the adsorption and subsequent decomposition of DMAB into elemental boron at the cathode during electrodeposition. However, introduction of the TiO₂ micro particles into the matrix of the NiB coating may be due to the effect of electrophoretic migration, forced migration and loose adsorption at the cathode. It can be observed that the addition of TiO₂ has led to a decrease in both nickel and boron content in the coating. However, their relative proportion is observed almost similar as compared to that of NiB coating (When the amount of TiO₂ is excluded). It can be said that the incorporation of TiO₂ results in the decrement of nickel and boron proportionately depending upon its co deposition efficiency.

Surface morphology

The smooth surface morphology of NiB coating may be due to the smooth finish of the support material which provides a uniform surface for the deposition of NiB coating. There is no preferential site for the deposition to take place and hence the deposition takes place uniformly throughout the exposed substrate material which results in an almost smooth coating. NiB coatings having greater than 4 wt. % of boron are amorphous and the amorphous nature may be due to grain refinement effect brought about by addition of boron [31]. It can be observed from the SEM micrograph that the grains are very fine to be observed clearly at the given magnification. The formation of globular clusters might be affected by many factors like the flow of nickel ions from the solution to the cathode, the stirring effect, the hydrogen evolution and its place of adsorption on the cathode surface, etc. The higher irregularity of NiB-TiO₂ coating may be because of co-deposition of the TiO₂ particles which being insulators generates a preferential site for nickel ion deposition [32]. The average smaller cluster size and the more protruding clusters in case of NiB-TiO₂ coating may be due to the co-deposition of TiO₂ particles which restrict growth of the existing protrusions and promote the formation and growth of newer clusters into the solution. The protruding clusters are also promoted by the fact that the ions from the solution get easily deposited on them owing to their access to a higher concentration of ions, lower travel distance by the ions and higher current densities on the protrusions.

XRD analysis

The XRD peak of NiB coating is very broad and broad peaks, also known as humps, are generally attributed to amorphous

structures or to nanocrystalline structures where the crystallite size is finer than 2 nm. Berkish have suggested that NiB alloys tend to develop a nanocrystalline structure for boron contents less than 8 wt. % and amorphous structure for boron contents greater than 20 at %. Since the XRD pattern of NiB exhibits a broad peak with a sharp tip, it could either mean a nanocrystalline structure with crystallite size finer than 5 nm or a combined amorphous and nanocrystalline structure. Considering the boron content (15.88 wt. %), it is more probable that the material has a mixed amorphous and nanocrystalline structure. The improvement in crystallinity of the NiB coating by addition of TiO₂ microparticles might be because the TiO₂ particles are negating the grain refinement effect of the boron by promoting the crystal growth of nickel in a particular direction. This is also believed to be the reason for (100) texturing of the NiB-TiO₂ composite.

Thermal stability

The DSC studies on the NiB and NiB-TiO₂ alloys reveal that addition of TiO₂ has not altered the thermal stability of the coatings significantly. An endothermic peak was observed at temperatures close to 375°C and this peak is the result of precipitation of NiB compounds. Systematic studies by Lee, have shown that precipitation of NiB compounds (Ni₃B) leads to the release of heat and the amount of heat released and the temperature at which the heat is released is related to the boron content [33]. An increase of boron content leads to easier precipitation of NiB compounds and this precipitation happens at a progressively lower temperature. However, the opposite has been observed in the present case. This might be because the difference in boron content is not significant (15.88 wt. % vs. 13.39 wt. %) between the two coatings or at this level of boron content, the kinetics of formation of Ni₃B is hardly affected. Prasad and Chokshi have also correlated the exothermic peaks in the DSC scans of electrodeposited Ni-1.5 wt. % P to the formation of Ni-P precipitates [34]. As boron contents of the NiB alloy are higher (15.88 wt. %) than that of the NiB-TiO₂ alloy (13.39 wt. %). The depth of the DSC peak corresponding to the NiB coating is higher than that of the NiB-TiO₂ coating due to higher heat generation. The finer crystallite size of the NiB alloy might also be contributing towards the higher depth of the DSC peak as the grain growth will occur at lower temperatures and will require more energy. The impact of boron content on the exothermic peak temperature can also be understood through the comparisons made by Shakoor in their study. They have found a mild secondary exothermic peak at 319°C and a primary exothermic peak at 361°C for NiB and a primary peak at 302°C and a secondary peak at 406°C for the NiB-Al₂O₃ alloy. The lower values of the primary endothermic peak temperatures observed by Shakoor could be attributed to the lower boron content of the alloy studied by them. Shakoor have studied alloys with boron content in the range of 6-7 wt. %, whereas in the present study the boron content is in the range of 13-16 wt. %. This comparison thus serves as a good validation of hypothesis that higher boron content lead to shifting of exothermic peaks to lower temperatures and reinforces our view that the DSC behaviour in our alloys is being controlled by the precipitation of NiB compounds [35,36].

Hardness

Since one of the primary driving forces for the development of nickel-based coatings is to utilize them as an alternative to hexavalent hard chrome coatings. It's of interest to compare the properties of the NiB and NiB-TiO₂ coatings to that of hexavalent hard chrome coatings. Figure 5 provides a comparison of the hardness of NiB and NiB comparing the hardness values of the different coatings is to develop an understanding of the performance of the coatings produced in this study *vis-a-vis* those from earlier studies. It can be observed from figure 5 that the coatings produced in this study are harder than most of the coatings reported earlier. Nanocrystalline nickel has the lowest hardness of the lot and has about (30-35% as per my observation) lower hardness than the hard chrome coating. The alloys of nickel such as NiP, NiB and NiW all provided hardness in the range 8 to 12 GPa comparable to that of hard chrome, albeit NiB produced in this study has marginally higher hardness than the hard chrome coating. However, the composites *i.e.* NiB with diamond, NiB-Al₂O₃ and NiB-TiO₂ provided significantly higher hardness than the hard chrome coating. Interestingly, the NiW-diamond composite had a lower hardness compared to the composites of NiB and this could be attributed to the lower hardness of NiW itself. Also, it is well known that it is difficult to incorporate a high concentration of diamond particles into the matrix by conventional electrodeposition process and thus the low concentration of diamonds combined with the low relative hardness of NiW explains the lower hardness of the NiW-diamond composites. The higher hardness of the composites can be attributed to the Orowan strengthening contribution obtained from the dispersion of the hard ceramic particles. The higher hardness of the NiB coatings produced in this study could be ascribed to its fine nanocrystalline structure.

Aqueous corrosion resistance

The linear potentiodynamic polarization studies indicated a distinct improvement in corrosion behavior of NiB-TiO₂ alloy *vis-a-vis* the NiB alloy. This improvement in corrosion behaviour of electrodeposited Ni based composites compared to the parent Ni alloy has been observed earlier in several studies. Krishnaveni have found improvement in corrosion behavior of NiB alloy by introducing Si₃N₄ precipitates into the matrix. The parent NiB alloy had a corrosion potential of -0.58 V vs. Saturated Calomel Electrode (SCE), whereas the Ni-B-Si₃N₄ alloy had corrosion potential of -560 mV vs. SCE. Similarly, the corrosion current density of the NiB alloy was approximately 3×10^{-2} mA/cm² while that of Ni-B-Si₃N₄ was 1.5×10^{-2} mA/cm². The marginal

improvement was attributed to the reduction in active corrosion area brought about by the inert Si_3N_4 precipitates. In current study, the corrosion current density of NiB alloy was found to be $1.7 \times 10^{-5} \text{ A/cm}^2$ while that of NiB- TiO_2 alloy was $1.1 \times 10^{-5} \text{ A/cm}^2$. Similarly, the corrosion potential of the NiB alloy was -500 mV vs. SCE while that of the NiB- TiO_2 composite was -250 mV vs. SCE. The substrate on other hand had a corrosion current density of $5 \times 10^{-5} \text{ A/cm}^2$ and corrosion potential of -670 mV vs. SCE. The large crystallite size, residual stress in the structure may be reason for the higher corrosion resistance of NiB- TiO_2 Composite coatings. This large crystallite size prevents formation of corrosion active site cells on the surface of coating. The comparatively fewer corrosion cells which get formed on the surface gets are spread over the surface and hence produce a protective barrier with corroding solution. That's believed to be the reason for the comparatively less corrosion current produced in the case of NiB- TiO_2 composite coating. Also, compressive stress makes it difficult to enter inwards in the structure. While in the case of NiB coating the smaller crystallite size develops many corrosion active sites on the surface and hence is prone to corrosion. Negligible solubility of B in Ni gives rise to higher heterogeneity in the structure which helps in the galvanic cells formation in the structure. Steel is more prone to corrosion out of the NiB- TiO_2 , NiB; the higher corrosion resistance in the case of NiB compared to steel is because of the obstruction inherited by the boron or any of its compounds to restrict the corrosion. Improved corrosion resistance shown by the NiB substrate compared to steel substrate has been also reported earlier.

Conclusion

NiB and NiB- TiO_2 were produced by the electrodeposition technique. X-ray diffraction studies revealed the very fine nanocrystalline structure of NiB *vis-a-vis* its composites. However, the addition of TiO_2 did not modify the thermal stability of the coatings as was evident from the DSC studies. There was a distinct improvement in the hardness, elastic modulus and corrosion resistance of the TiO_2 containing coating compared to the parent NiB coating. The improvement in hardness and elastic modulus is attributed to the fine distribution of the TiO_2 particles that provide Orowan strengthening while the improvement in corrosion performance is due to the reduction of active corrosion sites brought about by the inert TiO_2 .

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

USW performed all the experimental work, collected and analyzed the data and wrote the first draft of the manuscript. RN Approved the final version of the manuscript. AQM, RN revised the manuscript and approved the final version of the manuscript. AMSH and AKP conceptualized and designed the work.

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