

TRIBO-MECHANICAL CHARACTERIZATION OF ENB ALLOY COATINGS: EFFECT OF HEAT-TREATMENT TEMPERATURE AND SODIUM BOROHYDRIDE CONCENTRATION

Manik Barman, Tapan Kumar Barman, Prasanta Sahoo

Department of Mechanical Engineering, Jadavpur University, Kolkata, India

Abstract. *Previously electroless Ni-B (ENB) coatings were analyzed and optimized based on various coating parameters. However, variation of nano-indentation behaviour like nano-hardness, elastic modulus and scratch hardness variation with bath composition and heat treatment temperature has not been reported earlier. An attempt has been made to explore the same in the present study. ENB coating layers are deposited on AISI 1040 steel specimen with varying concentration of sodium borohydride (NaBH_4) and heat-treated at 350°C, 450°C and 550°C to investigate the related effects. Nano-hardness and elastic modulus of as-coated specimens are found to improve with NaBH_4 concentration due to increased boron content and nodule size. Both nano-hardness and elastic modulus are observed to improve further upon heat treatment because of incorporation of various boride phases leading to compact morphology and increased size of the nodules. Scratch hardness value also increases with NaBH_4 concentration and it improves further upon heat treatment and reaches to its maximum at 450°C due to presence of compact and hard Ni_2B phase. Compact homogeneous surface morphology enhances the friction and wear behaviour of the heat-treated coatings even though surface roughness deteriorates after heat treatment.*

Key words: ENB, Heat-treatment, COF, Wear, Nano-hardness, Micro-scratch

1. INTRODUCTION

ENB alloy coatings are known to have improved tribological behaviour due to their cauliflower-like surface morphology which helps to improve frictional behaviour by reducing the real contact area [1, 2]. ENB coatings also enhance the surface hardness of mild steel substrate [3, 4]. The coatings have also been investigated on the basis of different parameters like plating rate, thickness, surface morphology, surface roughness, surface hardness, tribological behaviour etc. [3, 4]. It was observed that the coating's behaviour

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Corresponding author: Prasanta Sahoo

Department of Mechanical Engineering, Jadavpur University, Kolkata 700032, India

E-mail: psjume@gmail.com; prasanta.sahoo@jadavpuruniversity.in

depend on coating composition which is a function of bath composition [3, 4] and bath temperature, pH etc. The amount of boron in the ENB coated films is seen to depend on coating bath temperature [3,4] and NaBH_4 concentration [3, 5]. Therefore, a small change in coating bath composition may modify the coating characteristics due to change in surface morphology, phase structure and coating composition.

ENB coatings exhibit crystalline structure at low boron content [3] while it turns to a combination of amorphous-crystalline structures with increase in boron content till medium level [3,5]. The same phase structure further transforms into X-ray amorphous with the increasing amount of boron [3]. Therefore, the phase structure is a function of boron content. It was also reported that phase transformation of ENB coatings starts at around 300°C [6-8]. The amorphous or amorphous-crystalline phase structure transforms into crystalline phase with the incorporation of Ni, Ni_2B , Ni_3B due to heat treatment [6,7]. Corrosion performance of the coatings with crystalline structure is seen to be better than amorphous structure [3]. Hardness and wear resistance were seen to improve with the increase in boron content [3] possibly due to compact, homogeneous surface morphology and amorphous phase structure. Hardness and wear resistance get improved further after heat treatment [9] with the incorporation of various hard phases like Ni, Ni_2B , Ni_3B [6,10]. Hardness of ENB coatings having boron content up to 6% does not differ much while it gets improved upon rise in boron content beyond 6% [11]. Moreover, hardness increases upon heat-treatment till 450°C . The same also increases with heat treatment duration. The transformation of hard Ni_2B , Ni_3B phases may be attributed for increase in hardness upon heat treatment [12].

Binary alloy coatings are deposited with the addition of various hard particles like Mo, W and investigated for evaluation of their characteristics [10,13,14]. Incorporation of hard nano or micro sized particles into metal matrix may modify the coatings characteristics. Different nickel based binary and ternary coatings are deposited with hard nano-particles like ZrO_2 , Al_2O_3 to improve the surface hardness and elastic modulus through grain refinement [15]. Hardness, corrosion performance and wear resistance of nano-composite coatings get improved due to addition of nano-particles like TiO_2 , ND etc. into Ni-B matrix [16].

Therefore, it is apparent that ENB coating characteristics depend on its surface morphology, phase structure and chemical composition. These parameters vary with the concentration of bath constituents. Hence, the chemical content, surface morphology and phase structure may be altered by varying the bath composition. The operating conditions of the bath also influence the coating composition, plating rate, morphology and phase structure. ENB coatings have been investigated to study the mechanical behaviour using nano-indentation technique at a fixed concentration of coating bath parameter. The surface morphology and phase structure also change with heat treatment which also impacts coating characteristics. The impact of reducing agent concentration and heat treatment temperature on nano-hardness, elastic modulus and scratch hardness has remained unexplored so far. Thus, an attempt is made now to deposit ENB coatings by varying the reducing agent (NaBH_4) concentration and then subjecting it to heat treatment at different temperatures to evaluate the related effect on nano-hardness, elastic modulus and scratch hardness. Modification of surface morphology and phase structure with variation in bath composition and heat treatment temperature has been correlated with nano-hardness, elastic modulus and scratch hardness behaviour.

2. EXPERIMENTAL DETAILS

2.1 Coating deposition procedure

ENB coatings are deposited on AISI 1040 steel substrates. AISI 1040 steel contains 0.32-0.43 wt.% C, 0.10-0.25 wt.% Si, 0.68-0.85 wt.% Mn, 0.03 wt.% S, 0.06 wt.% P and the remainder is Fe. Square samples of size 15mm x 15mm x 2mm are used for the testing of mechanical properties. Cylindrical samples of size ϕ 6mm x 3cm long are employed for friction and wear tests. The specimens are smoothed and cleaned using soap water and rinsed in acetone to remove any oily substance. Rust and oxide layers are removed by 50% HCl solution. Finally, the smooth, defect-free specimens are emersed into chemical bath for coating deposition. Steel surface is catalytically active to start the coating deposition process. However, the specimens are dipped into lukewarm PdCl₂ to accelerate the deposition process further. A 200 ml coating solution bath is used for coating deposition. Coating bath load is maintained within the range of 28.5 to 31.1 cm²/L. In the current study, no mechanical or ultrasonic agitation is used. Alternatively, bath replenishment is chosen so that the coating bath stability and deposition rate is not hampered as well as the deposition of diffused layer does not take place due to the reduction of reactive species. The 200ml bath is replaced with another one after 2 hours as a measure of bath replenishment. Therefore, a constant time duration of 4 hours is applied to deposit ENB coatings on steel specimens. The coating bath contains NiCl₂ (20 g/l) and NaBH₄ (0.50, 0.80, and 1.10 g/l) as nickel and boron source in the solution, respectively. NaBH₄ concentrations of 0.50, 0.80 and 1.10 g/l are termed as low, medium and high concentrations in next sections. NaOH (40 g/l) and C₂H₈N₂ (59 g/l) are used as a buffer and complexing agent, respectively. PbNO₃ (0.0145 g/l) is utilized as a stabilizer. Coating bath temperature is maintained at around 95±2°C. On the other hand, bath pH is maintained at 12.5. After the deposition with varying NaBH₄ concentration is over, the specimens are heat-treated at 350°C (HT350), 450°C (HT450), 550°C (HT550) for 1 hour and cooled in the furnace itself.

2.2 Coating characteristics

Surface morphology of ENB coatings is analysed using SEM (Model: S3400N, Make: HITACHI, Japan) accompanied by a secondary electron detector. Elemental analysis of these coatings is done at an energy level of 10-15 KeV with the help of EDAX. The setup is equipped with a super ultra-thin window for effective transmission of low energy x-rays. The EDAX system has been calibrated with Si. The spectrum of the standard boron sample is compared with the as-deposited coated specimen spectrum to calculate the boron content [7, 17]. The XRD system uses Cu-K α radiation with 2 θ angle ranges from 20° to 90° and the scanning rate is kept constant at 0.02°/sec.

2.3 Friction and wear measurement

A pin-on-disc type multi-tribotester (Model: TR-20LE-CHM-400, Make: DUCOM, India) is employed for the analysis of tribological behaviour of the coated specimens under dry sliding conditions. The tribological tests are carried out as per ASTM standard G99-05 (Reapproved 2010). The cylindrical specimens of ϕ 6mm x 3cm in length are used for the tribo-tests. The rotating disc is made of EN31 (58-68 HRC) having diameter of 11.5cm and

thickness of 8mm. The cylindrical samples are pressed against the rotating disc with 50N of normal load. Sliding velocity is maintained as 0.3925 m/s for a travel distance of 471m and a track diameter of 6 cm. Friction force at the contact between coated surface and rotating disc is recorded in the attached computer. Mass of the specimen before and after each test is measured using a weighing balance having a precision of 0.01 mg. The difference between the two readings is the mass loss during tribo test. This mass loss is employed to calculate the specific wear rate. The following Eq. (1) is employed to determine the specific wear rate (W_s in Kg/N.m)

$$W_s = \frac{M}{S \times P} \quad (1)$$

where, M is mass loss in kg, S is travel distance in m, and P is applied load in N.

2.4 Mechanical properties

Nano-indentation tests are carried out using a nano-indentation test set up (NHT-1, CSM Make) provided with a diamond made triangular base pyramid shape Berkovich indenter. The maximum indentation depth is maintained as 500 nm [12]. The constant loading-unloading rate is 40 mN/min and idle time is 2 seconds. The system considers Oliver and Pharr method to estimate hardness and elastic modulus [12]. The maximum indentation depth is kept below 1/10th of minimum coating thickness to avoid the substrate effect on test results [6]. The coated surfaces are polished with ultra-fine diamond paste to avoid roughness effect on indentation test results. The tests are conducted for 3 different samples obtained from same bath composition and at 10 locations along a line on each sample. The average of these data is considered here.

Scratch hardness is measured using a micro-scratch test set up (Model: TR-101-IAS, Make: DUCOM, India) as per ASTM G171-03 standard. The test setup is provided with a diamond made Rockwell C type indenter and the indenter tip radius is 200 μm . The tests are conducted against an applied load of 20N and the scratch length is kept as 5 mm. The scratch velocity is kept constant at 0.1 mm/sec. The scratch width is measured at 10 different locations and the average of those values is used to calculate the scratch hardness. The following Eq. (2) is used to calculate the scratch hardness:

$$HS_p = 24.98 \frac{N}{X^2} \text{ GPa} \quad (2)$$

where HS_p is scratch hardness, N is applied load in gm and X is scratch width in μm .

3. ANALYSIS OF RESULTS

3.1 Coating characterization

The cross-cut thickness of ENB samples is measured using the SEM and the images are presented in Fig. 1. The minimum coating thickness is measured to be 13 μm at low NaBH_4 concentration [3]. The thickness values are measured to be 27.89 μm and 30.69 μm for medium and high NaBH_4 concentrations, respectively. This indicates an increasing trend

of thickness with NaBH_4 concentration as deposition time is 4 hours for all the samples. Higher concentration of NaBH_4 increases the reduction rate leading to increase in deposition rate leading to the increase in coating thickness. Similar increasing trend has also been reported earlier [4]. The coating thickness of $9\mu\text{m}$ to $22\mu\text{m}$ is observed within the borohydride range of 0.50 to 1 g/l [4].

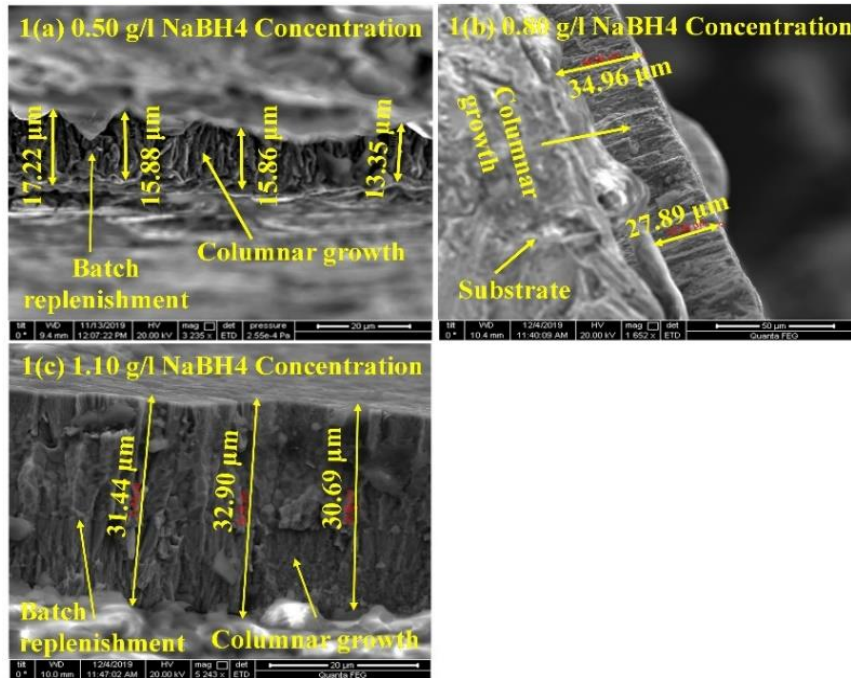


Fig. 1 SEM image of cross-cut thickness of as-deposited ENB coatings obtained at NaBH_4 concentration of, (a) 0.50 g/l, (b) 0.80 g/l and (c) 1.10 g/l

Boron contents in the coatings are found to be $3.5\pm 0.40\%$, $6.60\pm 0.50\%$ and $8.70\pm 0.40\%$ for coatings obtained with low, medium and high NaBH_4 concentrations, respectively [3]. Boron content is observed to increase with NaBH_4 concentration as reported earlier [7]. This agrees well with the current observation. The increase in NaBH_4 again enhances the reduction reaction leading to rise in boron content on coated layers. The coatings deposited with medium NaBH_4 concentration are found to possess 6.5%–7% boron which is in line with earlier observation [18].

Surface morphology of the ENB coatings has been displayed in Fig. 2 to Fig. 4. The SEM images of as-deposited specimens displayed in Figs. 2a, 3a and 4a show homogeneous distribution of nodules and uniform surface morphology throughout the working range. The coatings exhibit cauliflower or broccoli-like surface morphology in as-deposited conditions [1,2]. The nodules are observed to get separated and form broccoli-like surface morphology at higher concentrations and an increase in nodule size is also displayed in Fig. 4a. The broccoli-like surface morphology is usually formed with small

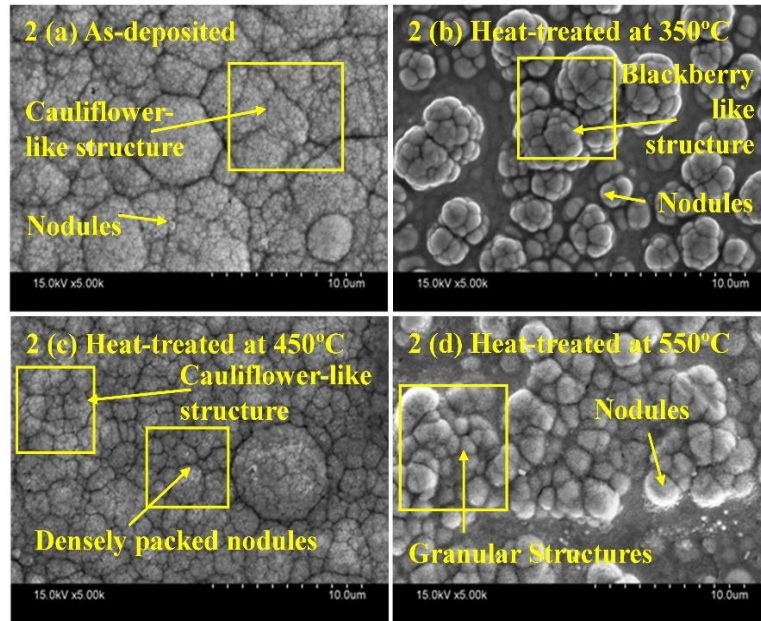


Fig. 2 SEM image of ENB coated surface for 0.50 g/l NaBH₄ concentration and, (a) as-deposited, (b) HT350, (c) HT450, and (d) HT550

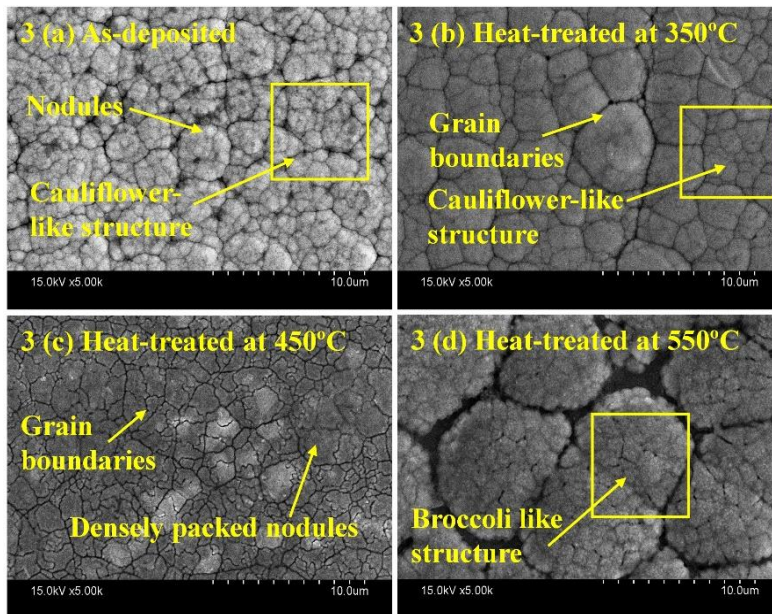


Fig. 3 SEM image of ENB coated surface for 0.80 g/l NaBH₄ concentration and, (a) as-deposited, (b) HT350, (c) HT450, and (d) HT550

granules [19]. The coatings displayed in Figs. 2a, 2c, 3a and 3c are observed to maintain the cauliflower-like surface morphology even after heat treatment. The coating deposition starts at the metal surface and accumulates vertically. This vertical deposition leads to columnar growth which dominates over horizontal growth [14]. Similar columnar growth may be seen in Fig. 1. Those columnar growths ultimately lead to cauliflower like surface morphology. The morphology displayed in Figs. 2b, 2d, 3d, 4b, 4c and 4d shows the transformation of cauliflower to nodular structure due to the interaction effects or fusion of grains which resemble a bunch of grapes or blackberry [19]. The coating growth is observed to result a nodular surface morphology which bears a likeness to a bunch of grapes or blackberry due to the interaction effect with the rise in increasing NaBH_4 concentration and due to heat treatment [19]. Fig. 3c shows the compact morphology with some prominent grain boundaries. The grains of the coatings get fused and become compact. But group-wise fusion makes some grain boundaries prominent.

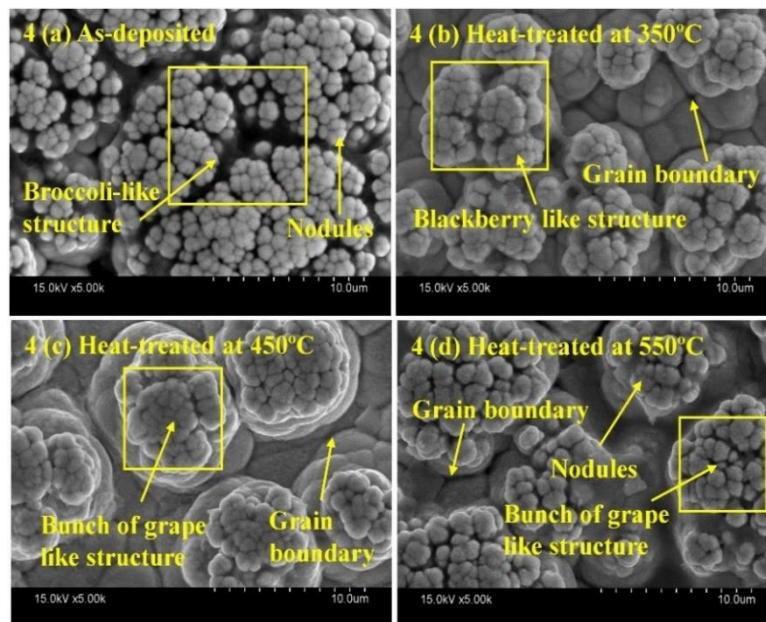


Fig. 4 SEM image of ENB coated surface for 1.10 g/l NaBH_4 concentration and, (a) as-deposited, (b) HT350, (c) HT450, and (d) HT550

The x-ray diffraction (XRD) patterns of the ENB coatings are displayed in Fig. 5. It clearly shows that the coatings obtained with low NaBH_4 concentration exhibit a single sharp broad peak at about 53° accompanied by a hump in as-deposited condition [11] which is an indication of the co-existence of amorphous and nano-crystalline structure [1,10,11]. Generally, coatings exhibit amorphous structure below 4.3% boron content [8,20]. A single hump only may be observed for coatings deposited with medium and high NaBH_4 concentrations in as-deposited condition [1,8,11]. The absence of a single broad crystallinity peak indicates the transformation of phase structure into amorphous structure due to a rise in boron content with NaBH_4 concentration [3,4].

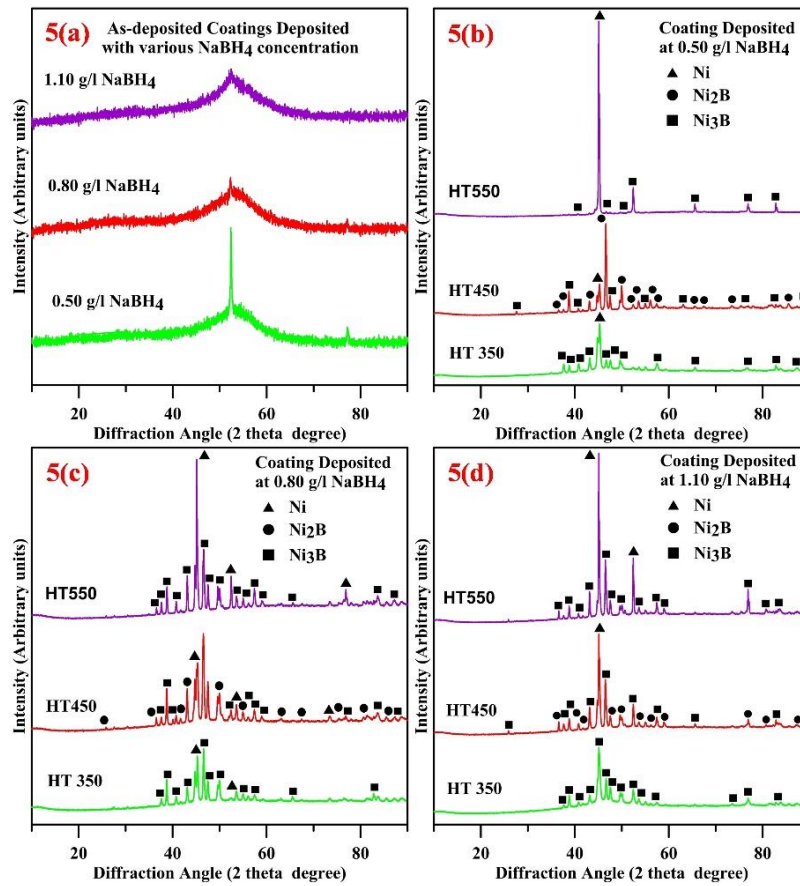


Fig. 5 XRD patterns of ENB coating in, (a) as-deposited, (b) deposited with 0.50 g/l NaBH₄ and heat-treated, (c) deposited with 0.80 g/l NaBH₄ and heat-treated, and (d) deposited with 1.10 g/l NaBH₄ and heat-treated

Crystallisation of ENB coatings starts just below 300°C of heat-treatment temperature [6,7]. The HT350 ENB coatings only exhibit crystalline peaks of Ni and Ni₃B for low to high NaBH₄ concentrations [6]. Precipitation of Ni and Ni₂B phases can also be observed with the dissolution of Ni₃B phases at higher temperatures [6] which may be the reason for the presence of Ni and Ni₃B crystalline phases only at 350°C. The presence of crystalline phase Ni₂B may be observed with Ni and Ni₃B at 450°C [6,21]. Similar results for coatings heat treated above 400°C was reported in previous studies [4]. The presence of high-intensity crystalline peaks in the XRD spectrums is the indication of phase transformation from amorphous to crystalline structure upon heat treatment [6,12]. Study shows the coatings with 1-4.5% boron content do not crystalline completely [4,8]. This may be the reason for the gradual increase in sharp and high-intensity diffraction peaks with heat treatment temperature and NaBH₄ concentration [4]. But ENB coatings do not contain Ni₂B phase at 550°C while the majority of the Ni₃B phases may be found besides Ni phase.

3.2 Mechanical properties

The nano-indentation test results are displayed in Table 1. ENB coatings are observed to enhance the hardness of steel [3,4]. From Table 1, it may be seen that the hardness and elastic modulus increase with NaBH_4 concentration in as-deposited condition [3]. The surface hardness of as-deposited coatings is seen to vary with boron content in coatings [11]. The boron content is observed to rise with NaBH_4 concentration [3,4]. Hence, nano-hardness also improves with NaBH_4 concentration, though it remains almost same till medium level. The hardness of the ENB coatings till mid boron is seen to remain almost same [11]. In this study, the boron content is found to be around 6.6% till medium level which comes under mid boron content coatings. The current study agrees well with previous literature [11]. The nano-hardness is seen to improve after heat-treatment throughout the working range. The precipitation of various hard crystalline phases leads to this improvement in surface hardness. The presence of hard, compact crystalline phase Ni_2B leads to the highest hardness value of low NaBH_4 coatings at heat treatment temperature of 450°C [6,12] as the Ni_2B phase is known to be more compact phase than Ni and Ni_3B [12]. The same decreases slightly upon further rise in temperature till 550°C due to absence of Ni_2B phase. The hardness of the medium and high NaBH_4 coatings improves with heat treatment temperature [12]. This improvement may be because of the addition of various crystalline phases which are reported earlier [4,8,22]. The coatings heat treated at 450°C contains Ni_2B phase [12] which is more compact leading to increase in surface hardness. It has been also reported earlier that the coatings with less than 4.5% boron content do not crystalline completely [2,8] which may be attributed to the lower hardness at low concentration and low heat treatment temperature. The hardness of the coatings obtained with medium and high NaBH_4 coatings increases with heat treatment temperature till 550°C possibly due to the hard crystalline phases as well as higher boron content.

The elastic modulus is seen to increase with grain size [23]. This may be the cause of the rise in elastic modulus value of as-deposited ENB coatings with NaBH_4 concentration. Elastic modulus of ENB coatings is found to be the functions of heat treatment temperature and duration [12]. The elastic modulus values presented in Table 1 show an increasing trend with heat treatment temperature. It was also reported earlier that the grain size increased upon heat treatment temperature and duration [12]. The grain size of the coatings increases with heat treatment temperature which may be the possible reason for improvement in elastic modulus [12]. Hence, the current study is in well accordance with the earlier reports [12]. The rise in elastic modulus is possibly because of addition of various crystalline phases which agrees well with previous studies as well [4,8,22]. The precipitation of various boride phases, as well as increased grain size, might have led to an improvement in the elastic modulus of the heat-treated coatings.

The calculated scratch hardness value is displayed in Table 1 which shows that it gets improved with NaBH_4 concentration in as-deposited condition. Similar to nano-hardness, the rise in boron content in the coatings may be the reason for this rise in scratch hardness. The scratch hardness value reaches its maximum at 450°C . The precipitation of the Ni_2B phase may be the reason for highest scratch hardness of the heat-treated coatings at 450°C [12]. Similar type of rise in nano-hardness may also be observed. The increase in nano-hardness and scratch hardness from as-deposited to heat treated at 450°C may be due to the transformation of various crystalline (Ni, Ni_3B) phases [9]. The scratch hardness decreases

upon further increase in heat treatment temperature at 550°C possibly due to presence of less compact phase Ni₃B phase instead of Ni₂B. Moreover, the clustered surface morphology with several prominent grain boundaries may be another reason for the decrease in scratch hardness at 550°C. The scratch hardness of the coatings in this current study is seen to be less relative to the as-deposited Ni-B-W [14]. The incorporation of tungsten into Ni-B matrix enhances the hardness due to solid solution strengthening of the coating matrix [14]. In this current study, the scratch hardness is found to improve with heat treatment temperature due to compact coating structure and precipitation of various crystalline phases but it is less than the as-deposited Ni-B-W specimens [14]. The improvement in scratch hardness is correlated with the strain hardening of coatings [14]. Nemane and Chatterjee [14] have found that scratch resistance increases in multi-pass scratch test due to strain hardening. The current investigation is carried out with single pass scratch test leading to lower scratch hardness value of heat-treated ENB coatings.

Table 1 Tribo-mechanical properties

Parameters	Hardness (<i>Hv</i>) Vickers	Elastic Modulus (<i>E</i>) in GPa	Scratch Hardness (<i>HSp</i>) in GPa	COF	Specific Wear rate (<i>Ws</i>) in x 10 ⁻⁸ Kg/N.m
Ni-B coatings with 0.50 g/l NaBH ₄ concentration					
As-deposited	388	82.70	0.80	0.46	23
HT 350°C	845	121	2.67	0.60	45.86
HT 450°C	1189	137	3.50	0.57	105.73
HT 550°C	1074	144	2.68	0.62	97.66
Ni-B coatings with 0.80 g/l NaBH ₄ concentration					
As-deposited	454.20	90.40	2.68	0.32	34
HT 350°C	992	131	3.71	0.77	33.97
HT 450°C	1156	178	4.43	0.72	19.10
HT 550°C	1208	195	3.45	0.78	11.08
Ni-B coatings with 1.10 g/l NaBH ₄ concentration					
As-deposited	867.90	121.30	3.50	0.16	80
HT 350°C	1030	144	4.90	0.65	16.14
HT 450°C	1244	195	6.35	0.70	17.83
HT 550°C	1388	218	4.00	0.67	39.92

3.3 Tribological behaviour

Average COF values of ENB coatings is also presented in Table 1. COF value of the as-deposited coatings decreases with the rise in NaBH₄ concentrations. Cauliflower like surface morphology is known to reduce friction between mating surfaces. This decrease in COF value with increased NaBH₄ concentration may be correlated with the cauliflower-like surface morphology and the increase in nodular size [3,4]. Bigger nodules of cauliflower-like morphology increase the lubricating action and hence it reduces the COF value [3,4]. The coated surface becomes rough due to an increased reduction rate with a rise in NaBH₄ concentration [1,24]. But the COF value is found to decrease at high NaBH₄ concentration coatings [24]. The surface roughness asperity has a tendency to break into

debris and fill the roughness valleys leading to smoothening of surfaces ultimately resulting in a reduction in average COF value [24].

The average COF value of all the heat-treated coatings is observed to increase relative to as-deposited conditions throughout the working range. The compact surface morphology leads to a slight reduction in COF value at 450°C. But the cluster aggregates forming a bunch of grapes like surface morphology at 350°C and 550°C may have led to a high average COF value for coatings deposited with low NaBH₄ concentrations. COF value of the coatings obtained with medium NaBH₄ concentration gets increased upon heat treatment possibly because of rough surface due to the exposure of prominent grain boundaries. The cluster formation may also be another reason for increase in COF value. The COF value of heat treated ENB coatings increases drastically at high level of NaBH₄ relative to as-deposited coatings. The surface roughness of ENB coatings obtained with high NaBH₄ concentration is normally high which increases further after heat treatment leading to high COF value. The roughness may become also high because of the nodule formation and fused together ultimately transforming to blackberry like surface morphology and making the surface rough. This rough surface is expected to increase the COF value but crushing the asperity peaks and filling the roughness valleys made the surface smooth. The smooth surface reduces the COF value and remain almost same throughout the heat treatment temperature range.

The specific wear rate values of the ENB coatings are presented in Table 1. It shows an increasing trend of wear rate for coatings obtained at low NaBH₄ concentration and heat treated till 450°C. The same decreases slightly at 550°C but remains higher than as-deposited one. The wear rate is found to decrease with the increase in surface hardness while it increases with rough surface [3]. Coatings with low boron content leads to lower hardness but roughness increased upon heat treatment due to increased nodule size which may be the reason for this increase in specific wear rate. While the wear rate is observed to decrease with heat treatment temperature for medium and high NaBH₄ coatings. In contrary to the friction coefficient, wear rate is observed to rise with NaBH₄ concentration in the case of as-deposited ENB coatings [11]. There is a chance of breaking the asperities of rough surfaces obtained from the high NaBH₄ concentration which led to an increment in wear rate [24]. The wear rate decreases for coatings obtained with medium and high NaBH₄ concentration with rise in temperature up to 550°C and that is possibly due to higher boron content as well as recrystallization of grains upon heat-treatment [8]. Boron content is observed to increase with NaBH₄ concentration [3,4,11] which may improve the surface hardness of the ENB coatings [3,4] and this may also be a possible reason for a decrease in specific wear rate.

SEM images of the worn-out zones of ENB coatings have been displayed in Figs. 6, 7 and 8. The Figs. 6a, and 8a shows the presence of wear debris on wear track which confirms the adhesive type wear mechanism of the as-deposited coatings [17,24]. Wear grooves may also be observed along the sliding direction which was caused by the repetitive nature of loading during the sliding [17,24]. Fig. 6b and 7a show the delamination of the upper layer of the coatings with ploughing at certain areas. While heat treated coatings possess rough surface. Those roughness asperities must have been crushed and ground severely. The wear debris is also found to be deposited along the sliding direction or attached to the sliding surface which acts as load-bearing areas leading to improvement in wear resistance with heat treatment temperature [8,11] and reduction in COF value sometimes [23]. Overall,

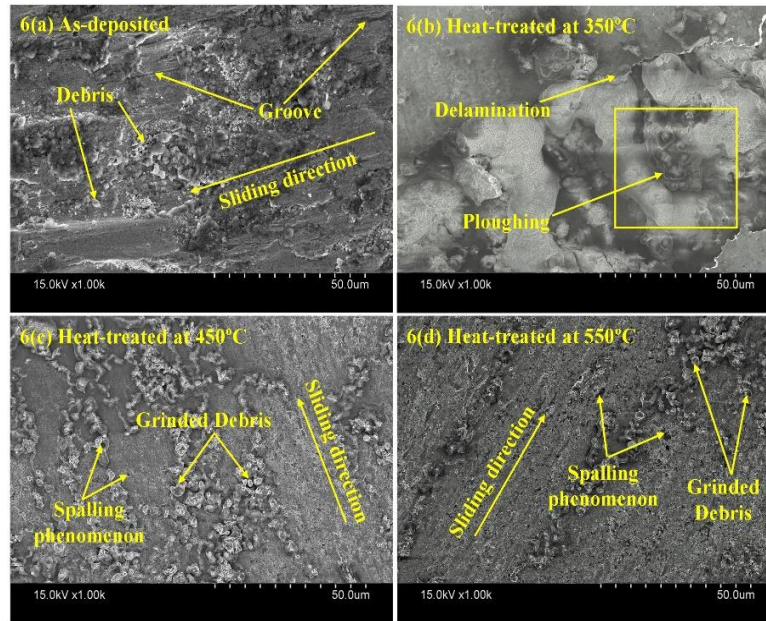


Fig. 6 SEM image of worn out ENB coated surface for NaBH_4 concentration of 0.50 g/l in (a) as-deposited, (b) HT350, (c) HT450 and (d) HT550

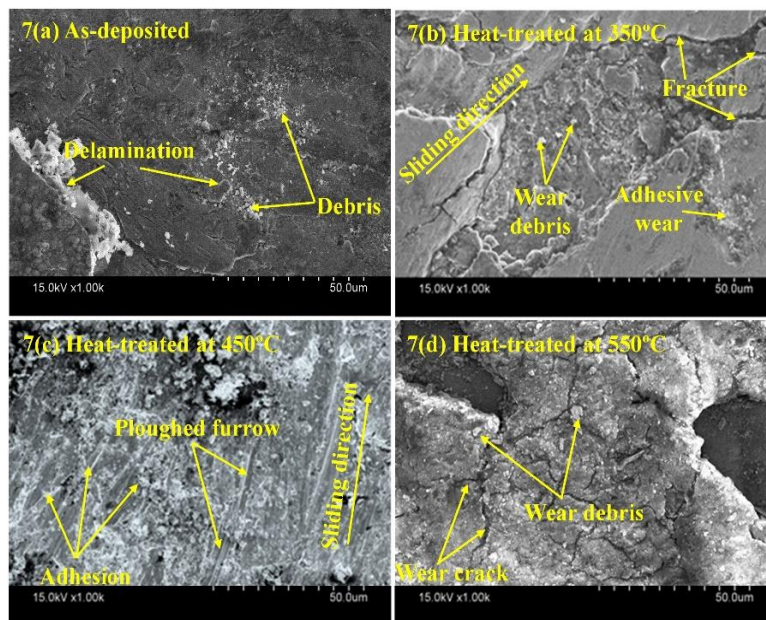


Fig. 7 SEM image of worn out ENB coated surface for NaBH_4 concentration of 0.80 g/l in (a) as-deposited, (b) HT350, (c) HT450 and (d) HT550

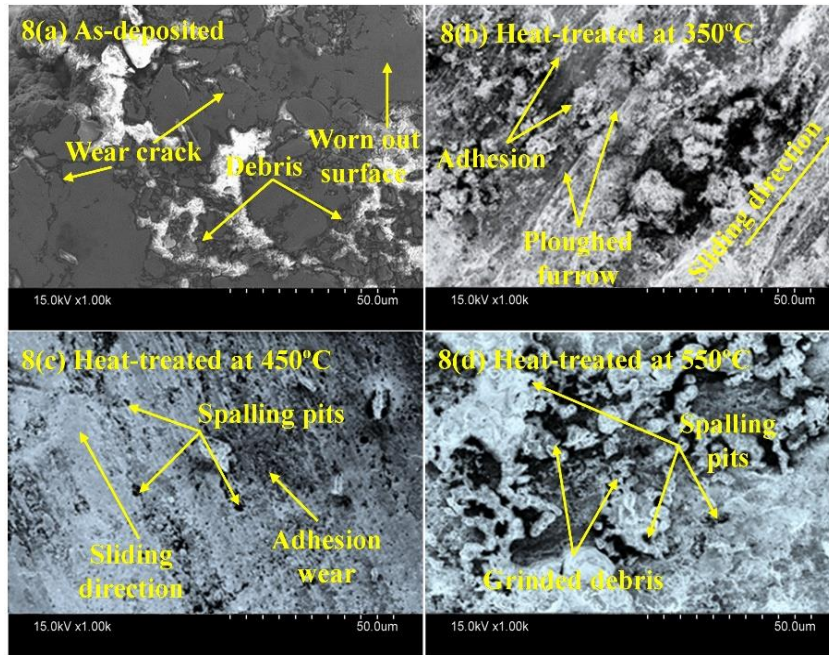


Fig. 8 SEM image of worn out ENB coated surface for NaBH_4 concentration of 1.10 g/l in (a) as-deposited, (b) HT350, (c) HT450 and (d) HT550

adhesive type of wear mechanism is observed to dominate for the borohydride reduced ENB coatings over delamination of layer and abrasive type wear mechanism. A significant amount of mass loss occurs at the beginning of sliding due to grinding of roughness peaks which leads to increase in higher wear rate. But debris also found to attach with the sliding surface which separates the counter surface during tribological tests [11]. This also may lead to reduction in specific wear rate of the heat-treated coatings [8]. There are some spalling phenomenon or pitting may also be observed along the sliding direction because of the ground debris and adhesive type wear. Therefore, the borohydride reduced ENB coatings in as-deposited and heat-treated condition predominantly exhibit an adhesive type wear mechanism.

The electroless nickel-based coating deposition method is widely used for surface modification. The electroless deposition processes suffer some issues to dispose the toxic elements used in this process. Some electroless coating bath uses PbNO_3 as stabilizer which is banned in many countries. Accordingly, concept of cleaner production using chemical vapor deposition, physical vapor deposition etc. are being practiced. Still, the electroless process cannot be overlooked because of their excellent tribological and mechanical behaviour. Hence, the researchers are working on to develop lead free bath [25,26]. Recently, several other stabilizers based on bismuth, tin are tried as replacement of lead based ones [27, 28]. Thus incorporation of the concept of cleaner production in electroless coating processes by making the coating bath eco-friendly is attracting substantial attention of researchers over the globe [29].

4. CONCLUSIONS

The outcome of the current investigation is summarized as given below:

- The amorphous or mixture of amorphous nano-crystalline structure of as-deposited ENB coatings are transformed into crystalline phase structure throughout the working range.
- The nano-hardness value is also observed to improve with NaBH₄ concentration because of increased boron content. The same is also improved further with heat treatment temperature due to precipitation of hard crystalline phases like Ni, Ni₂B, Ni₃B and compact surface morphology.
- The elastic modulus is also increased with NaBH₄ concentration in as-deposited condition possibly due to the rise in nodular size. The nodules get enlarged further and form clustered morphology leading to further increase in elastic modulus upon heat treatment.
- The COF of as-deposited coatings is observed to follow reverse trend with NaBH₄ concentration rise. The COF values of heat-treated coatings remain higher than the as-deposited one irrespective of NaBH₄ concentration and throughout the temperature range.

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