



Article

Wear Behavior of Friction Stir Processed NAB Alloys in Marine Environment

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Abstract

Nickel Aluminum Bronze (NAB) alloy specimens subjected to Friction Stir Processing (FSP) with and without particulate addition were subjected to tribological testing in a reciprocating sliding tester which can perform sliding test on specimens immersed in sea-water. Stainless steel ball was slid against flat coupons of NAB as cast, and Friction-Stir-Processed NABs, under sea-water to study the wear performance considering their prospective use in marine bearing applications. The wear expressed in terms of the wear scar area measured using an image processing method indicates that the performance of the Friction-Stir-Processed NABs in sea-water environment is inferior to that of the un-processed NAB, even though the processed NABs have relatively superior hardness. While wear tests in dry condition indicate that the wear resistance for the friction stir processed samples is high, under saline environment the trend was found to be reversed, as their wear resistance was found to be low. The reduction in wear resistance in sea-water is explained in terms of the (electrochemical) corrosive wear mode being active in the saline medium. The surface damage as revealed from the SEM characterization of wear scars were found to correlate with the experimental deductions.

Keywords

NAB, friction stir processing, tribocorrosion

1 Introduction

Nickel Aluminum Bronze (NAB) is a copper based alloy with Nickel (~7%), Iron (~7%) and Aluminum (~13%) as main alloying elements, together with other elements like Manganese. Due to superior mechanical properties and corrosion resistance, it is widely used in marine applications, and in aerospace industry and architecture.

Friction Stir Processing (FSP) is a materials processing operation in which a rotating non-consumable tool is thrust into the workpiece (Fig. 1), causing localized heat generation, plastic flow, and churning, altering the microstructure and properties of the workpiece material. The process causes high strain, strain rate, and temperature gradients within the narrow zone subjected to FSP. FSP has been found to improve the mechanical properties of NAB alloys [1-3] and particulate addition into the processing zone during the FSP process has been found to enhance them [4, 5]. In a recent development [6], a novel in-situ method for incorporating nanoscale ceramic particles during FSP has been found to improve the micro-hardness significantly. While processing, this alloy using FSP, the ceramic phase was introduced as an organic-polymer precursor (a class of silicon based polymer known as polysilazanes) that would undergo

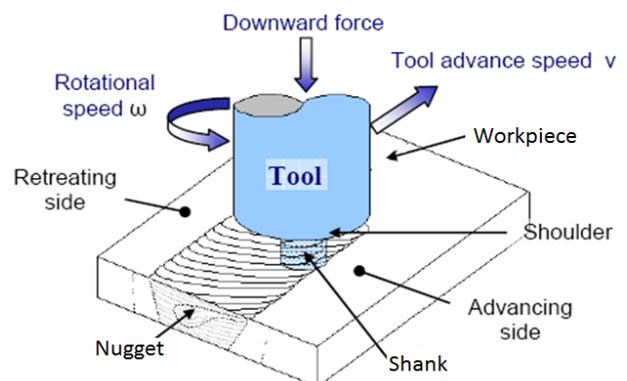


Fig. 1 Schematic of the friction stir process

pyrolysis at higher temperatures thereby converting it into a ceramic phase, known as polymer-derived ceramic (PDC) which was found to result in increased hardness (details of the process can be got from [6]).

Previous studies related to wear behavior of NAB alloys concentrated on the synergistic effect of erosion and corrosion suffered by NAB alloys in saline environment, erosion-corrosion

studies by using short term electro chemical techniques, impingement studies and long term immersion tests [7-9]. But, wear studies coupled with corrosion effects related to FSP processed NAB alloy in marine environment has not received much attention. Since the earlier researches [7-9] are mainly related to the erosive wear behavior, it would be worthwhile to investigate the wear behavior of FSP processed NAB and its composite under metal-to-metal sliding conditions in sea-water, considering the prospective use of this alloy for bearings in marine environment.

The ideal way of performing a test on any engineering system would be to conduct the test in the real life set-up, as it is, but except in some exceptional situations it is not possible to do so due to various reasons (from the point of view of destruction and damage that happens due to the test, accessibility, cost, ease of modification of the set-up to suit different test conditions, environmental challenges, controllability of the test etc.).

The main challenge of laboratory testing of tribological interactions is to simulate the mechanical, physical, chemical, thermal and environmental conditions as would exist in the real life scenario, which the laboratory test is trying to mimic. If not perfect, the laboratory test should capture all essential features of the reality which would make the predictions that evolve out of the tests reliable and valid. In the context of the present problem which tries to analyse the wear of NAB alloys in sea water environment, if we examine the possibility of performing the tests in a standard tribological testing equipment like scratch tester, pin-on-disk (POD) wear and friction tester, four ball tester etc., performing the tests in these conventional equipment would not be welcome due to the following reasons: (1) the tribological interaction should happen within sea water and (2) it is difficult to prepare/manufacture disc of FSP processed alloys for a POD nor is it easy to or make a pin of desired contour using conventional machining of these FSP processed sample. Though it is not impossible, cost would be a prohibitive factor, considering the number of tests that would be required.

To fulfil the conditions listed above, it was planned to make a test set-up which would enable wear testing inside sea-water, which would lessen the burden of specimen preparation and which would render testing in an ergonomically comfortable way.

2 Experimental procedure

The wear tester used is shown in Fig. 2. In the setup, the sample and the ball sliding (reciprocating motion having sliding speed 0.004 m/sec and frequency of 40 strokes/min at 30°C) over it are immersed in the liquid tray (a rectangular tub with a volume of 800 ml). The tester can hold flat specimens of size 25 × 25 × 5 mm. Stainless steel ball (SS316) having 15.85 mm diameter is chosen for the experiments, which slides against the flat coupons of NAB alloy specimens. Each experiment was conducted by letting a virgin surface of the ball sliding against the flat specimen which meant that a previously scratched surface of the ball was not made to slide again. The selected sea water was collected from the sea in West Hill, Kozhikode (Calicut), Kerala, India. Experiments were run at 1 kg load and for duration of 15 minutes, which were chosen based on the service performance of the machine, after some trial runs. This loading (1 kg) would correspond to a Hertzian contact pressure of 589 MPa, which is well above the yield point value of the sample NAB (295 MPa). All tests are conducted at 30°C. Sea

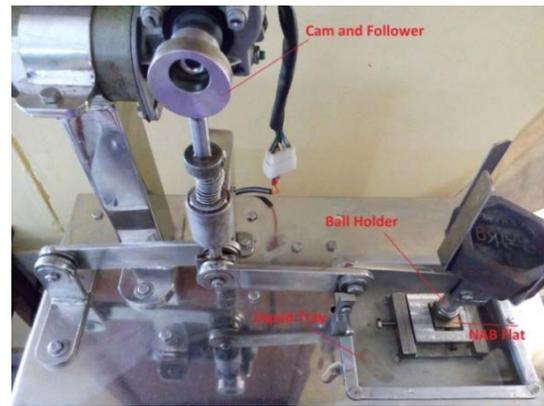


Fig. 2 Wear tester machine

Table 1 Details of sea water characterization

Parameter Value	Parameter Value
PH	7.76
TDS (Total Dissolved Salts)	19,500 ppm
Salinity	25,900 ppm

water used for the investigations is characterized for PH, TDS and Salinity (Table 1).

Particulate added samples were prepared by performing FSP on the plates reinforced with SiCN cross-linked polymer powder (10 µm), three passes of FSP were carried out on a five-axis friction stir welding machine [6] at a tool rotation speed of 1500 rpm and traverse speed of 25 mm/min. Three different samples were tested- (1) particulate added FSP processed NAB (denoted PNAB), (2) no particulate added, but FSP processed NAB (denoted FNAB) and (3) NAB received as cast and no FSP processed and no particulate added (denoted NAB). Samples were tested in three different environments namely 1. Sea water 2. Purified (Millipore) water and 3. Dry (Unlubricated). The micro-hardness was measured on the transverse cross-section of the samples using a micro Vickers hardness tester with a load of 100 g for 10 s. The Scanning Electron Microscope (SEM) was used to capture the microstructure of the NAB (as cast), FNAB and PNAB composite samples.

The measurement of the wear scar area were calculated with the help of digital processing of the captured images through ImageJ software (photogrammetry technique) [10, 11].

3 Results

Figure 3 shows the microstructure; the PDC particles are distributed in the NAB matrix for the PNAB sample (Fig. 3 (c)). Microhardness of the PNAB is 324 HV (Fig. 4), while it is 202 HV for the unprocessed sample (NAB). This hardness increment is due to the grain refinement as well as PDC particle distribution in the matrix which will pin the grain boundaries and increase the strength (Fig. 3 (a)-(c)).

Table 2 gives the measured wear scar area for dry condition. The wear is less for the FSP processed samples (FNAB and PNAB). Under this (dry) condition, the wear correlates (inversely) with the hardness (Fig. 4) of the samples. Higher the hardness, lesser is the wear (scar area), which is a trend matches with the classical Archards wear model. Adhesive wear (due to the interface being dry) and the characteristic squeal noted during these tests and abrasive wear (third body abrasion) as suggested by the scoring marks in the wear scar (image not

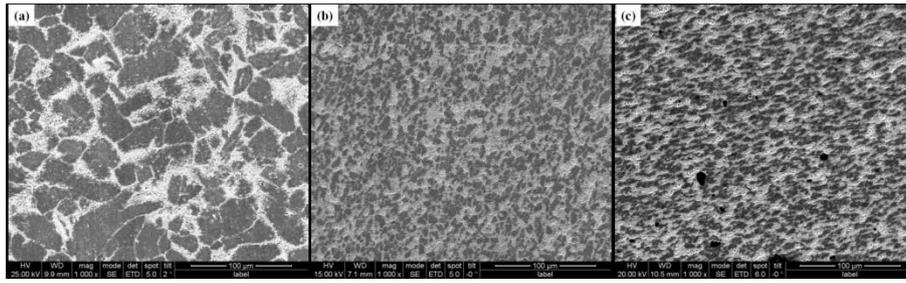


Fig. 3 SEM images showing microstructure of the samples used: (a) NAB, (b) FNAB and (c) PNAB

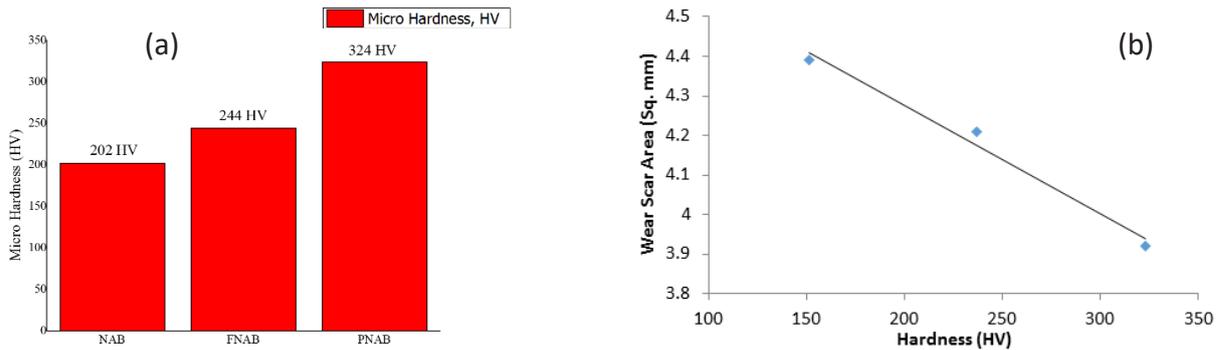


Fig. 4 (a) Comparison of micro-hardness of the NAB samples, (b) Relationship between wear scar area (dry condition, 1 kg., Load, 15 minute test) and the hardness values of the specimens

Table 2 Wear Scar areas for tests in dry condition. Changes in wear scar area with unprocessed NAB chosen as reference. Load = 1 kg., Duration = 15 minutes

Sample	Wear Scar Area (mm ²)	% Change in Wear Area	Scatter (Percentage deviation from mean)
NAB	5.96	0.00%	-7.61% - 10.99%
FNAB	5.41	-9.22%	-10.01% - 8.33%
PNAB	4.58	-23.15%	-15.95% - 12.63%

Table 3 Wear Scar areas for tests in sea water. Changes in wear scar area with unprocessed NAB chosen as reference. Load = 1 kg., Duration = 15 minutes

Sample	Wear Scar Area (mm ²)	% Change in Wear Area	Scatter (Percentage deviation from mean)
NAB	3.95	0.00%	-15.97% - 19.75%
FNAB	5.42	37.21%	-8.21% - 9.26%
PNAB	5.18	31.13%	-6.40% - 7.36%

shown) would be the dominant wear modes in this condition.

The wear scar areas measured from experiments in sea water are given in Table 3. Contrary to the previous trend which showed lesser wear for the processed samples in dry condition, the trend is reversed in the sea-water test, the wear is more for the processed samples. The difference in trend observed in sea-water tests can be explained if we consider the fact that the (electrochemical) corrosion of FSP processed alloy was found to be low as compared to the unprocessed sample as reported by Ni et al [12], their study being based on Electrochemical Impedance Spectroscopy (EIS) and on the polarization curve. Ni et al [12] ascribes this to two reasons: (1) due to the increase in Gibbs Free Energy introduced by the Friction Stir Processing resulting in severe plastic deformation and residual stress in the processed samples, which was also reported in Refs. [13-15] who found that the corrosion increases due to residual stress:

the increased Gibbs free energy being characteristic of a state with increased chemical reaction affinity and hence reduced corrosion resistance and (2) due to a reduction in grain size due to the FSP process, increasing the number of grains and hence the grain boundaries. SEM micrographs of the samples used for the present experiments (Fig. 3 (c)) are suggestive of this grain size refinement due to FSP processing. Grain boundaries are areas prone to initiate the preferential attack, as they are regions of increased energy, which would suggest that the attack due to corrosion would be more in the processed sample. The (electrochemical) corrosion wear would therefore be active in the saline medium and would cause more damage on the processed samples, which leads us to conclude that mechanical damage as well as corrosive wear would have a synergistic effect in the wear under these conditions. The summary is that the wear resistance of the processed samples as compared to the

Table 4 Wear Scar areas for tests in purified water. Changes in wear scar area with unprocessed NAB chosen as reference. Load = 1 kg., Duration = 15 minutes

Sample	Wear Scar Area (mm ²)	% Change in Wear Area	Scatter (Percentage deviation from mean)
NAB	6.57	0.00%	-7.87% - 8.88%
FNAB	5.57	-15.22%	-3.20% - 4.58%
PNAB	5.70	-13.24%	-16.22% - 10.36%

Table 5 Wear Scar areas for tests in sea water. Changes in wear scar area with unprocessed NAB chosen as reference. Load = 3 kg., Duration = 60 minutes

Sample	Wear Scar Area (mm ²)	% Change in Wear Area	Scatter (Percentage deviation from mean)
NAB	10.47	0.00%	-4.84% - 8.43%
FNAB	10.72	2.28%	-7.51% - 8.86%
PNAB	11.16	6.59%	-5.19% - 5.77%

unprocessed one is found to be less in sea-water. If the above hypotheses are true, then if we let it wear in a medium where the electrochemical aspect would be dormant (like Millipore water), then this trend should disappear; Table 4 shows the wear data in purified water. It can be seen from Table 4 that the wear of the processed samples in purified water is less than that of the unprocessed sample and following a trend like the dry tests, which may be construed to be due to the electrochemical mechanism being dormant in purified water, due to relatively very less electrical thermal conductivity of purified water (Millipore), as opposed to sea-water.

4 Discussion

This confirmatory test ascertains the arguments that the electrochemical corrosion would lead to increased wear of these alloys when they are electrochemically coupled with a counterface like stainless steel which is higher up in the Galvanic Series [16] in an electrolytic environment like sea water. SEM images from wear tracks from these tests are given in Fig. 5 ((a)-(c)). The SEM images are illustrative of the surface damage mechanisms hypothesized in the previous sections. The presence of the wear-debris found on the surface for the FNAB and PNAB samples (Fig. 5 (b) and (c)) due to combined erosion and corrosion in sea water contributes to the severity of the plowing during sliding and consequently the wear is more for these samples. It is also noticeable from the microscopy that the reinforcement particles are de-bonded and appears as free particles in PNAB (Fig. 5 (c)), which would also contribute to plowing, because they are hard abrasives. The reason(s) for the de-bonding (at the interfacial bonding between the matrix and the reinforcement) in PNAB under this environment are a matter for further detailed analysis and is beyond the scope of this paper. A repeat of the sea water tests was done at a higher load and longer duration also (3 kg Load and 60 minutes' duration). The results are given in Table 5. The wear performance of the processed samples is less than that of the unprocessed one, a trend found from the previous experiment using 1 kg load and 15 minutes' duration (Table 3).

SEM images from wear tracks from the higher load and longer duration tests under sea water are given in Fig. 6 (a)-(c). These SEM images are characteristic of surfaces which have suffered relatively more surface fatigue (as compared to those in Fig. 5) due to prolonged sliding, repeatedly over the same tracks at higher loads. The SEM image of the plain NAB sample (Fig. 6 (a)) shows severely strained surface, but the surface

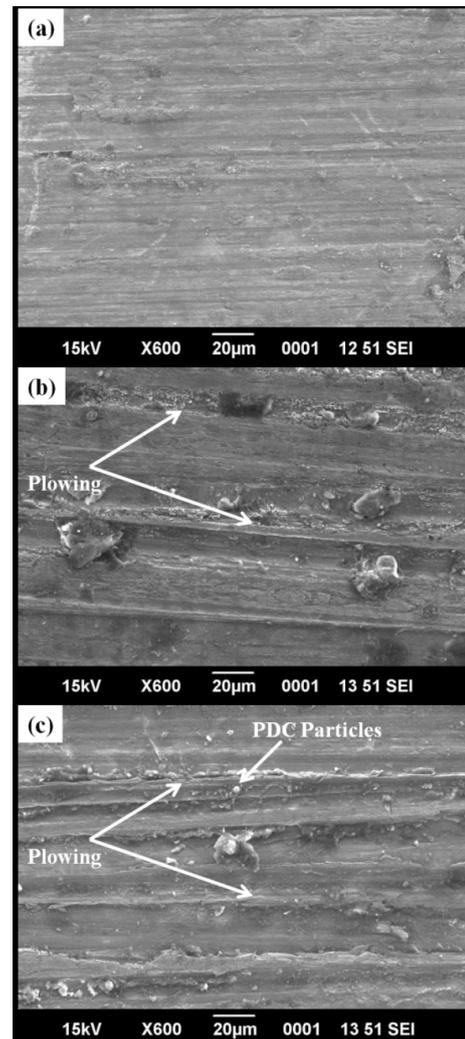


Fig. 5 SEM images of (a) NAB, (b) FNAB and (c) PNAB surfaces tested in sea-water (1 kg, 15 minutes) respectively

damage being relatively not so severe. On the other extreme, the worn surface morphology (Fig. 6 (c)) of the processed sample (PNAB) shows severe damage with plowing, micro-cutting, and pitting suggesting combined effect of (electrochemical) corrosion and mechanical damage. The case of FNAB (Fig. 6 (b)) is intermediate to these extreme cases. The severity registered in the SEM images is in accordance with the wear characterized

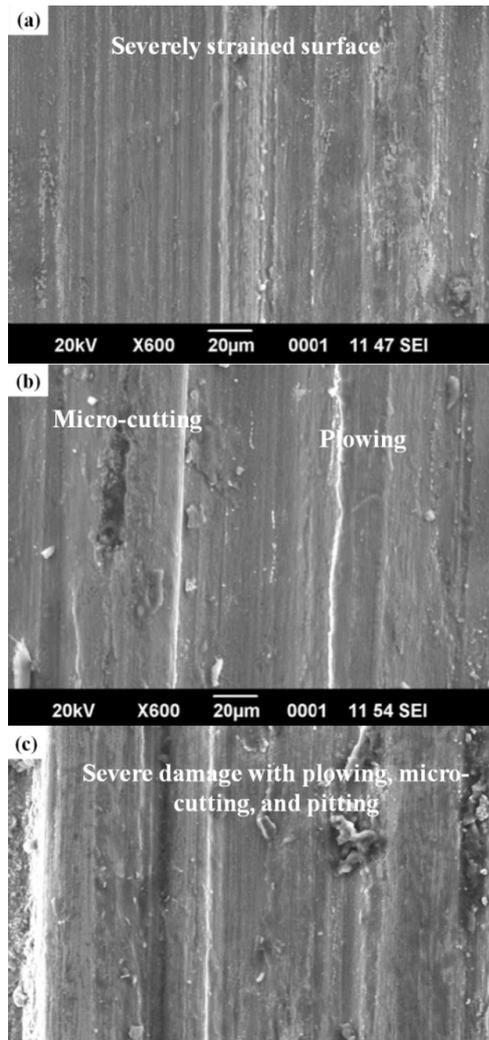


Fig. 6 SEM images of (a) NAB, (b) FNAB and (c) PNAB surfaces tested in sea-water (3 kg, 60 minutes) respectively

in terms of the wear scar area reported for the sea water tests (Tables 3 and 5).

Comparison of the trends from the wear tests under the three environments (Tables 2, 3 and 4), shows that the magnitude of wear under purified water was found to be more as compared to the other two cases, followed by dry tests and tests in sea water, in that order. This is because for the dry tests (exposed to ambient), the formation of the oxide layer happens readily, while this formation is impaired for tests under purified water using Millipore water. Presence of the oxide layer is expected to offer better resistance to abrasion, and hence the wear is found to be less for the dry test as compared to tests under (purified) water. An increase in wear scar area is obtained for the processed samples in seawater, as compared to rubbing in purified water environment. This could be due to the higher concentration of ions in seawater resulting in the formation of such compounds are quick and hence the corrosive mode of wear would be prevalent under such conditions; similar observations with aluminum alloys have also been reported [17-19]. Even though abrasive wear and fatigue wear too would contribute to wear due to the reciprocating mode of sliding discussed in this paper, the dominant mechanism would be due to the corrosive effect. In short, the net wear would be a synergistic effect of all these modes, with corrosive wear being the most significant one. It seems to be plausible because a significant level of squeal and vibration was noticeable while using purified water for the present wear tests, while it was absent for tests under sea-water. Fig. 7 indicates the overall consolidated results of variation of wear scar area vs environments and materials.

5 Conclusion

1. FSP processing improves the mechanical-strength (hardness), their use in marine systems would require a thorough reconsideration (when coupled with a relatively passive metal system like stainless steel).

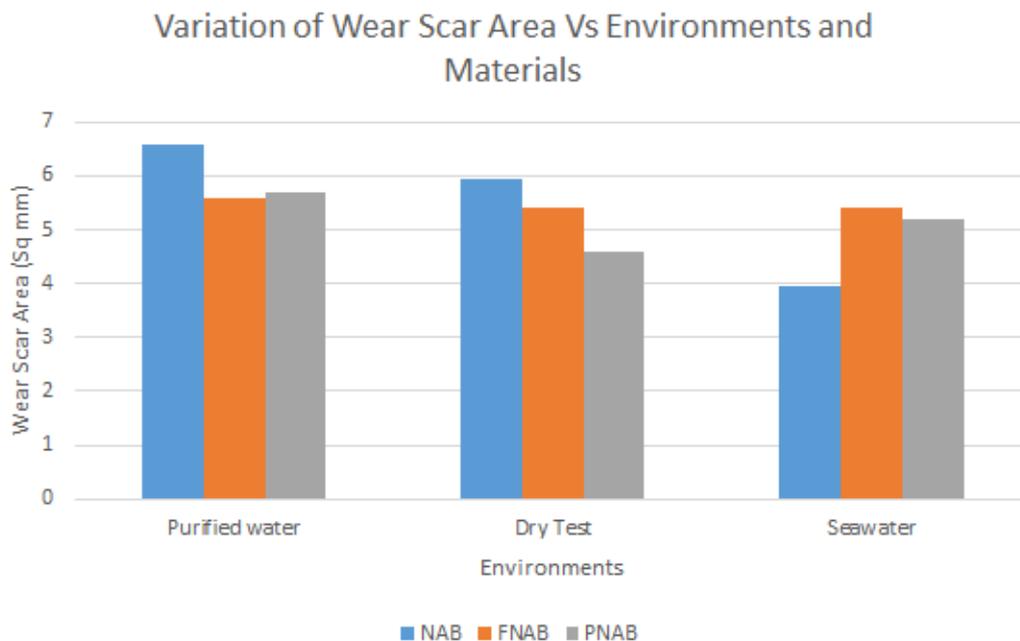


Fig. 7 Variation of wear scar area vs environments and materials

2. Wear in one medium can be catastrophically different from wear in another environment, once again as demonstrated by the present experiments.
3. Selection of materials for wear resistance should be based on tests which can simulate actual contact conditions as well as the environment to the maximum extent possible, if the results from the tests are to be extrapolated for real life applications.
4. Even though the effect of processing (FSP and particulate addition) improves the mechanical strength (hardness) of the NAB samples, the present analyses indicate that the FSP processing do not improve their wear performance under marine environment, but, reduces it.
5. The reduction in wear resistance of the FSP processed samples in sea water (compared to the unprocessed NAB sample) is attributed to the contribution due to electrochemical corrosion, which increases due to (i) severe plastic deformation and residual stress in the processed samples, and (ii) reduction in grain size due to the FSP process, increasing the number of grains and hence the grain boundaries. The microstructure and residual stresses influences the wear of NAB alloys to a large extent, as confirmed by previous investigators.
6. While the dry wear of the materials considered seem to be governed by the mechanical damage due to adhesion and abrasion, the wear under sea-water condition is influenced by mechanical damage as well as electrochemical corrosion. The SEM images correlate with the experimental deductions.
7. The contribution from the environment (sea water) in initiating the electro-chemical mode is confirmed by performing the tests under purified (Millipore) water, which demonstrated that the electrochemical action is dormant in purified water.

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