Wear properties of Ti–13Zr–13Nb (wt.%) near β titanium alloy containing 0.5 wt.% boron in dry condition, Hank’s solution and bovine serum

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ABSTRACT
The effect of heat treatment on the microstructure, hardness and sliding wear behaviour of Ti–13Zr–13Nb (wt.%) containing 0.5 wt.% B (TZNB) has been studied and compared with that of Ti–13Zr–13Nb (wt.%) (TZN) alloy. The wear properties were tested in dry condition and in simulated body fluid (Hank’s solution and bovine serum) to understand the effect of different medium on wear behaviour of the TZNB alloy. Depending on the heat treatment condition the microstructure of the alloy consisted of α/martensite and TiB in β matrix. In general, the hardness of all the heat treated samples varied in a narrow range and in most of the cases addition of boron to the TZN alloy decreased the hardness. Almost all cases, no significant variation of the wear rate in dry condition with heat treatment was observed. Compared with the wear rate in dry condition, the wear rate in Hank’s solution of the all the TZN samples increased substantially. Moreover, the wear was found to be most severe in bovine serum. Addition of boron to TZN alloy did not result in any improvement in the wear resistance in all the media studied.

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1. Introduction
Friction wear of implant materials is a major clinical problem [1]. The wear of prosthetic components generates debris, which cause adverse cellular response and inflammation, eventually leading to implant loosening and pain in the body. The presence of particulate corrosion and wear products in the surrounding tissues of the implant may result in a cascade of events leading to bone loss and ultimately to failure of the implant [1–6]. Titanium and several of its alloys are used as traditional biomaterials because of their excellent combination of corrosion resistance, biocompatibility and mechanical properties [1,7,8]. However, poor tribological properties of titanium and its alloys reduce the service life of the implants significantly. Titanium alloys show relatively poor wear resistance in articulating conditions. Therefore, recent focus has been on improving the wear resistance by proper surface modification techniques and/or by reinforcing the matrix with some hard precipitates [8]. Also, proper evaluation of the wear characteristics of biomedical titanium alloys in simulated body fluids (e.g. Ringer’s solution, Hank’s solution, bovine serum etc.) is essential.

Interstitial elements are extremely potent strengtheners of titanium alloys because of their ability to pin dislocations [9]. Although the influence of oxygen and hydrogen content on phase transformation, microstructure, mechanical properties and wear behaviour of titanium alloys has been reported [10–12], the effect of boron on the mechanical properties and particularly wear behaviour of titanium alloys has not been thoroughly investigated yet. Reinforcing the soft matrix of titanium alloys (including new generation β-Ti alloys) with hard ceramic precipitates such as borides offers the possibility of substantially enhancing the wear resistance of these composites [13]. Among many possible reinforcement compounds for titanium-matrix composites, TiB is the most promising one due to its high elastic modulus, similar density with Ti alloys, and excellent interfacial bonding with titanium matrix [14–17].

Ocelik et al. [18] reported that TiB reinforcement in α ± β type Ti–6Al–4V alloy by laser cladding process results in an improvement in the tribological properties of the composite in oil bath. Samuel et al. [13] observed an improvement in wear resistance of laser deposited boride reinforced β-Ti alloy composites (TiB/Ti–Nb–Zr–Ta alloy) in dry condition when compared with Ti–6Al–4V ELI. However, they did not study the wear properties of the composites in simulated body fluids. Also, a detailed study on TiB reinforced near β titanium alloys is lacking.

Among the several techniques available to synthesize metal-matrix composites (MMCs), the solidification process is attractive due to its simplicity, economy and flexibility. Small addition of boron to titanium alloys leads to formation of strong and stiff titanium-boride (TiB) phase that precipitates in situ during solidification [19].

In our previous study, the effect of heat treatment on the microstructure, hardness and sliding wear behaviour of Ti–13Zr–13Nb (wt.%) has been investigated [20]. In the present study, the
possibility of improving the wear properties of this alloy through hard particle reinforcements has been explored. Accordingly, TiB reinforced near-β titanium alloy was prepared by addition of small amount of boron that forms in situ TiB precipitates through solidification process. The wear properties of this composite in air and simulated body fluids was studied and compared with those of the Ti–13Zr–13Nb alloy. The effect of boron on mechanical and corrosion properties of titanium alloys has been reported elsewhere [21].

Laboratory wear tests were conducted to assess the wear properties of boron containing alloy and compared it with that of boron free TZN alloy. This test does not exactly reproduce the actual conditions in the human joint which is rather complicated and not completely understood [22]. Nevertheless, they are useful for predicting the wear behaviour and performance of the material in vivo and are widely used for first-level evaluation of the material and characterization of the wear behaviour [12,22–30]. Such tests are also valuable for comparison of different materials, heat treatment and surface treatment procedures.

Many different types of wear testing machines are used to study the wear behaviour of materials for orthopaedic use. These include ring-on-conforming block, pin-on-disc, disc-on-plate, ball-on-flat, etc. [22]. All these testing methods employ a simple geometry which does not exactly reproduce in vivo conditions in the human joint which is rather complicated and not completely understood [22]. For pin-on-disc machine either plastic or metal pins are used. This set up has an advantage of simplicity of surface pressure calculation and the modest load gives high pressure at the contact surface as may be found in some prostheses and loading situations. Pin-on-disc wear testing machine is therefore extensively used for evaluating the wear characteristics of implant materials [13,18,24,28,31–33].

The conditions for laboratory wear tests of implant materials have been spelt out by Dumbleton [22]. Both dry and wet wear tests have been described. Though dry wear tests do not replicate the actual conditions in the human body, they are performed to highlight the effect of the lubricants. A number of lubricating liquids has been listed for wet tests; these include distilled water, saline, Ringers or Hank’s solutions. Many different types of wear testing machines are used to study the wear behaviour of materials for orthopaedic use. These include ring-on-conforming block, pin-on-disc, disc-on-plate, ball-on-flat, etc. [22]. All these testing methods employ a simple geometry which does not exactly reproduce in vivo conditions in the human joint which is rather complicated and not completely understood [22]. For pin-on-disc machine either plastic or metal pins are used. This set up has an advantage of simplicity of surface pressure calculation and the modest load gives high pressure at the contact surface as may be found in some prostheses and loading situations. Pin-on-disc wear testing machine is therefore extensively used for evaluating the wear characteristics of implant materials [13,18,24,28,31–33].

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2. Experimental

Ti–13Zr–13Nb–0.5B (TZNb) alloy (compositions in wt.%) was prepared by arc melting with a non consumable tungsten electrode in a vacuum arc melting unit supplied by Vacuum Techniques Pvt Ltd, Bangalore. The melting chamber was first evacuated to less than 5 × 10⁻⁶ mbar and then flushed with high purity argon and evacuated again; the chamber was finally back-filled with the same gas before melting. Before melting of the alloy, a piece of pure titanium was melted as getter. The ingots were turned over and remelted at least six times in order to attain homogeneity of the alloy, a piece of pure titanium was melted as getter. The ingots were subsequently cooled with high purity argon and evacuated again; the chamber was finally back-filled with the same gas before melting. Before melting of the alloy, a piece of pure titanium was melted as getter. The ingots were turned over and remelted at least six times in order to attain homogeneity of the alloy, a piece of pure titanium was melted as getter. The ingots were turned over and remelted at least six times in order to attain homogeneity and microstructure. Three or four small buttons were remelted together and cast into ingot (approx. 40 g) in the same melting unit.

Boron has negligibly small solubility in Ti [34,35] and therefore, it was assumed that the addition of 0.5 wt.% boron to the TZN alloy would not change the transformation temperature substantially. Hence, the same heat treatment schedule that was applied to TZN alloy and reported by Majumdar et al. [20] was followed for the present TZNb alloy also. The work primarily aims at synthesis of Ti–13Zr–13Nb/TiB composite and proper design of the processing and heat treatment schedule of the material in order to produce an appropriate microstructure to provide suitable mechanical and wear resistance properties for implant material because microstructure of a material plays an important role in determining its properties. Desired microstructure can be obtained through thermo-mechanical processing and heat treatment operations. In case of two phase titanium alloys consisting of α and β phases, the properties of the alloys depend to a great extent on the amount, morphology and distribution of these phases [36]. Depending on the deformation temperature, thermo-mechanical work can produce either dynamically recrystallized equiaxed structure or a structure that consists of elongated grain in the direction of working [37]. In the present study, the samples were hot rolled at 800 °C (above β transus) and at 650 °C (below β transus).

In case of rolling at higher temperature it was expected that a dynamically recrystallized equiaxed structure would form. During hot working below β transus, α phase was expected to nucleate during the process of plastic deformation and the microstructure would contain a work structure. The solution treatment temperature and the rate of cooling to ambient temperature determine the volume fraction, size and shape of α and β phases [37]. Holding the alloy above or close to β transus temperature (800 °C or 700 °C in the present study) dissolves all or most of the alpha that develops during thermo-mechanical work while holding below the β transus temperature (650 °C in the present work) permits the matrix to retain most or the entire alpha that develops during thermo-mechanical work. The nature of the secondary α that forms during cooling from solution treatment temperature to room temperature is determined by the cooling rate. If the alloy is cooled very slowly (furnace cooling) the adjustment of volume fraction of α phase occurs by migration of the existing primary α/β interface [36]. Relatively fast cooling (air cooling) results in the formation of transformed β type structure. The relative volume fraction of primary α and transformed β can therefore be adjusted by solution treatment temperature and subsequent cooling rate. On the other hand, rapid cooling (water quenching) from the solution treatment temperature produces a non-equilibrium metastable phase called martensite if the partitioning effect does not enrich the β phase by β stabilizing elements. Small equilibrium amount of fine α phase can be precipitated in the matrix through controlled decomposition of martensite by aging treatment [37].

The ingot was given 30–40% reduction by groove rolling at two different temperatures (800 °C and 650 °C) and then air cooled to room temperature. The hot rolling temperatures were selected in such a way that it was above the β transition temperature in one case (800 °C) and below that temperature in another (650 °C). The hot rolled samples were solution treated at 800 and 650 °C for 1 h in dynamic argon atmosphere; this was followed by furnace cooling (FC), air cooling (AC) or water quenching (WQ). Water quenched samples were aged at 500 °C for 5 h.

Room temperature X-ray diffraction analysis was carried out in a Philips, Holland, PW 1710 X-ray Diffractometer with Cu Kα radiation at 40 kV and 20 mA. The scanning rate was kept at 3°–2θ/min, from 2θ= 20° to 100°.

Optical microscopy and electron microscopy were used for microstructural, wear surfaces and wear debris examination of the heat treated samples. For these purposes, scanning electron microscope, FEI Nova Nanolab 200 with FEG-SEM column operating at 20 kV using the secondary electron (SE) and backscattered electron (BSE) imaging modes, scanning electron microscope (SEM) (Model: JSM-5800, JEOL, Japan), operating at 20 kV voltage and JEM 2100 (JEOL, Japan) high resolution transmission electron microscope operated at an acceleration voltage of 200 kV were used. The
composition of the wear debris was determined by using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) on a scanning electron microscope (SEM) (Model: JSM-5800, JEOL, Japan), attached with Energy Dispersive X-ray (EDX) system (Model: ISIS 300 Oxford Instruments Limited, UK). The operating voltage of the SEM was 20 kV. For chemical analysis of the debris, a number of regions were examined in order to have an average composition. The composition was scaled to Ti±Zr±Nb±Fe=100 wt.% as suggested by Samuel et al. [13], because, the boron content in the alloy cannot be quantified by EDS. The polished samples were etched with Kroll’s reagent (10 vol.% HF and 5 vol.% HNO3 in water). Hardness of the pre-polished samples was measured at 10 kg load using a Vickers hardness tester (VM 50, Fuel Instruments & Engineers Pvt. Ltd., India); an average of ten readings was taken.

Sliding wear test was started at ambient temperature (30±2 °C) using a pin-on-disc wear testing machine supplied by Ducom, Bangalore. The disc was made of hardened high chromium steel having a hardness of Rc 69. The wear samples were prepared in the form of a cylindrical pin (8 mm diameter and 25 mm long) by machining from rolled bars, which were then heat treated as described above. Prior to the wear tests, the pin and the disc were polished metallographically to a roughness (Ra) level of 0.15–0.17 μm and 0.4–0.55 μm, respectively. Tests were carried out in dry condition as well as in wet conditions. Wet wear tests were carried out with Hank’s solution and with bovine serum. As discussed earlier, both these lubricating agents are commonly employed as model fluids for simulating human body fluid conditions [6,22–30]. Freshly prepared Hank’s solution was used for each experiment in the present investigation; it had the following chemical composition (values in g/l): 8 g NaCl, 1 g glucose, 0.4 g KCl, 0.35 g NaHCO3, 0.14 g CaCl2, 0.1 g MgCl2·6H2O, 0.06 g Na2HPO4·2H2O, 0.06 g KH2PO4 and 0.06 g MgSO4·7H2O [30]. The pH of the solution was maintained at 7.4.

Loads acting on human joints vary considerably from joint to joint. For a particular joint, it varies with time during the loading cycle (e.g., from “heel strike” to “toe off” during walking) and with loading rate (e.g., with pace (slow, normal or fast) of walking) [22,38]. It has been reported that the stresses in the living joints are of the order of 1 MPa [22]. Gispert et al. [26] used a normal pressure of 0.88 MPa in the contact zone to study the wear behaviour of prosthetic TiN coated stainless steel/ultra high molecular weight polyethylene (UHMWPE) tribological pair. Consistent with these reports, a normal load of 50 N (equivalent to a nominal contact pressure of 1 MPa) was applied to the specimen. A linear sliding speed of 1 m/s was maintained. Tests were continued up to a sliding distance of 2000 m; this was sufficient for attainment of steady state situation in all the cases. Wear rate, in the steady state, was computed by the rate of height reduction of the pin. The height reduction data were converted into volume loss by multiplying it with the area of cross section of the test pin. Wear surfaces, wear debris and subsurface were examined using scanning electron microscopy (SEM) and optical microscopy.

Fig. 1. Backscatter SEM micrographs of the TZNB alloy deformed at 800 °C and solution treated at 800 °C for 1 h followed by air cooling.

Fig. 2. (a) Bright field (b) dark field TEM micrographs and (c) selected area diffraction (SAD) patterns of the TZNB alloy deformed and solution treated at 800 °C followed by air cooling.
3. Results and discussions

3.1. Microstructure

Optical microstructure of TZN alloy after different heat treatment schedules was discussed in [20]. Addition of boron to TZN alloy led to the formation of titanium boride (TiB) precipitates in the matrix. SEM micrograph of the TZNb alloy shown in Fig. 1 revealed that addition of 0.5 wt.% B to TZN alloy resulted in the formation of dispersed precipitate particles of TiB. The majority of the boride precipitate particles show an acicular (needle like) morphology with lengths varying in the range of 5–10 µm with some particles being even larger than that. High resolution transmission electron microscopy results presented in Fig. 2 revealed the presence of TiB particles with orthorhombic B27 structure which belongs to ‘Pnma’ space group in α–β matrix. This is the equilibrium structure of TiB [39].

In the case of TZNb samples deformed and solution treated at 800 °C, the optical microstructure was found to be similar to that of the TZN alloy as described in detail by Majumdar et al. [20] when similar heat treatment was given. The β phase transformed to α phase on slow cooling (furnace) through the transus. The optical microstructure consisted of a basket-weave structure (Widmanstätten lath like α) formed from prior β grains (Fig. 3a). Multiple variants of α lath were observed within prior β grains. In air cooled sample, fine α–β structure was observed within prior β grains (Fig. 3b). Water quenching from a solution treatment temperature of 800 °C resulted in formation of martensite with some amount of retained β phase (Fig. 3c). Aging at 500 °C for 5 h after quenching from a solution treatment temperature of 800 °C transformed the martensite into α and β phases and produced fine distribution of globular α along the pre-existing martensite plates (Fig. 3d). Apart from the formation of titanium boride (TiB) precipitates in the matrix, boron had only a marginal effect on the overall microstructure of the samples which were deformed and solution treated at 800 °C. Thus, air cooled and aged samples showed somewhat coarser α phase. The TiB precipitate can be clearly observed in the optical microstructure of the water quenched sample shown in Fig. 3c.

In the case of TZNb samples solution treated at 650 °C after deformation at 800 °C or 650 °C, presence of primary α and transformed β/retained β along with TiB particles was observed for air cooled, water quenched and aged samples. Furthermore, relatively coarser primary α phase was observed in the optical microstructure (Figs. 4 and 5) when compared with similarly heat treated TZN samples [20]. Among all the samples heat treated in this condition, the size of the α phase was the largest in the aged sample and it was the smallest in the water quenched sample. The tendency towards the formation of coarse primary α growth is more pronounced for the samples solution treated at 650 °C than at 800 °C. The solubility of boron in titanium is negligible [34], it has been found to be only 0.05 wt.% or less in the temperature range of 700 °C–300 °C [35]. Hence it is expected that entire amount of B precipitates out as boride particles. Analysis of optical micrographs indicates that the growth of primary α is enhanced by the presence of boron in the alloy which is more pronounced in the case of samples solution treated below β transus (Figs. 4 and 5). Banerjee et al. [34] have shown that addition of 2 wt.% boron modifies the microstructure of the matrix of Ti–6Al–4V alloy. The morphology of a large number of α particles was shown to change from Widmanstätten lath type to equiaxed shape. Equiaxed/globular α usually forms in thermomechanically processed α + β titanium alloys. In the case of LENS™ (laser engineered net shaping) deposited Ti–6Al–4V–2B alloy, however, equiaxed α is formed without any mechanical working.

Fig. 3. Optical microstructures of the TZNb alloy deformed at 800 °C and solution treated for 1 h at the same temperature followed by (a) furnace cooling, (b) air cooling, (c) water quenching and (d) aging at 500 °C for 5 h after water quenching.
during the processing, which is attributed to the presence of TiB precipitates that act as nucleation sites for α [34]. Thus, in the present study, it can be concluded that the matrix microstructure is altered slightly in boron containing alloy, because of the presence of boron.

In all the TZNB samples, presence of orthorhombic titanium boride (TiB) precipitates in the matrix is evident from the XRD patterns shown in Figs. 6 and 7. The peaks of other phases observed in XRD pattern of TZNB samples are same as those of similarly heat treated TZN samples [20].

3.2. Hardness

In general, no significant variation of hardness with respect to different heat treatment conditions was observed except for the water quenched sample that was deformed and water quenched from 800 °C. Moreover, addition of boron to TZN alloy did not improve the hardness of TZNB alloy (Fig. 8) when compared with the hardness of similarly heat treated TZN alloy [20]. In contrast, in all cases, except water quenched samples, a decrease in hardness was observed. In general, a similar trend was observed in the case of deformation at 800 °C or 650 °C and solution treatment at 650 °C.

Although it was expected that the presence of hard TiB precipitate would increase the hardness of all the TZN samples, the hardness of only water quenched sample increased and that of air cooled and aged samples decreased. This can be explained by the fact that only 0.5 wt.% boron was added and this by itself has no substantial effect on the hardness. On the other hand, boron changes the morphology of the α phase and enhanced its growth during slow cooling and aging [34]. It is believed that the lowering of the hardness in boron containing alloy during air cooling and aging is due to the growth of the α phase. The decrease in hardness due to growth of α is larger than the increase in hardness due to presence of small amount of TiB particles and hence an overall decrease in hardness was noticed. In the case of water quenched sample, rapid cooling rate during water quenching prevents the growth of the α phase and thus the increase in the hardness of the water quenched sample can be attributed to the presence of TiB particles in the matrix.

3.3. Wear characterization

During the wear tests, the temperature at the articulating surfaces increases rapidly at first and then it attains a steady value. The wear rate was estimated from the rate of height loss or height reduction of the pin in the steady temperature range. Thus, the measurement of the height loss of the pin is not affected by thermal expansion due to gross temperature change during the test and is entirely due to wear [20]. Three samples were tested for each set of parameters. The wear rate was calculated from the slope of the volume loss of the pin vs. sliding distance plot assuming a simple linear relationship between the two and the data are presented as specific wear rate in unit of m²/N. The slope was estimated at 99% confidence level.

The wear behaviour of TZNB alloy in dry medium, in Hank’s solution and in bovine serum is presented in Figs. 9–11 respectively. In the case of dry wear, no significant variation of the wear rate with heat treatment was observed. Compared with the wear rate in dry condition, the wear rate of the all the heat treated TZNB samples increased substantially in Hank’s solution and it increased further in bovine serum. In the case of samples deformed and solution treated at 800 °C, no substantial variation of the wear rate with heat treatment was observed in both the media. However, for the samples solution treated at 650 °C after deformation at 800 °C or 650 °C, the air cooled and water quenched samples showed higher wear rate than aged sample. Moreover, the wear loss of the water quenched sample is higher than the air cooled sample.
The wear behaviour of TZN alloy after similar sets of heat treatment was presented earlier [20]. A comparison of wear properties of the presently investigated TZNB alloy with that of the TZN alloy is now being presented to understand the effect of boron on wear behaviour of TZN alloy.

Addition of boron to TZN alloy did not significantly affect the dry wear behaviour of the samples deformed and solution treated at 800 °C when compared with boron free TZN alloy [20]. However, the aged...
sample showed a decrease in wear. On the other hand, an increase in wear rate in dry condition was noticed in boron containing alloys deformed above and below the β transus and solution treated at 650 °C (Fig. 9a). Among all the TZNB samples tested in dry condition, the highest wear rate was observed for the sample which was deformed and solution treated at 800 °C followed by water quenching and aging.

In Hank's solution, compared with the TZN samples [20], the TZNB samples showed a substantial increase in the wear rate in samples deformed and solution treated at 800 °C followed by furnace cooling, air cooling or water quenching and aging (Fig. 10a). However, water quenched sample showed relatively small increase in wear rate. Similarly, in the case of samples deformed at 800 °C or 650 °C and solution treated at 650 °C, the wear loss of the air cooled and water quenched samples increased with the addition of boron. However, aging of the water quenched TZNB samples after deformation at 800 °C or 650 °C and solution treatment at 650 °C did not appreciably change the wear resistance when compared with the similarly heat treated TZN samples.

In bovine serum, for a particular solution treatment temperature, both TZN and TZNB alloys showed similar wear behaviour when subjected to similar heat treatment condition (Fig. 11a and Ref [20]). In most of the cases, no significant change in wear rate was found after addition of boron. However, TZNB samples deformed and solution treated at 800 °C followed by air cooling and water quenching showed a decrease in wear rate and the sample deformed at 800 °C and solution treated from 650 °C followed by air cooling exhibited an increase.

In general, the overall trend of the variation of the wear rate of TZNB alloy with respect to heat treatment was similar to that of TZN alloy [20]. Compared with the dry wear tests, wet wear tests of TZNB alloy exhibited a substantial increase in wear rate just like TZN alloy.

Fig. 9. Wear behaviour of TZNB alloy in dry condition. Samples were deformed at 800 °C or 650 °C followed by heat treatment under different conditions: (a) wear rate, (b) coefficient of friction and (c) temperature.

Fig. 10. Wear behaviour of TZNB alloy in Hank’s solution. Samples were deformed at 800 °C or 650 °C followed by heat treatment under different conditions: (a) wear rate and (b) coefficient of friction.
TZNB alloy also showed higher amount of material loss during wear testing in bovine serum than in Hank's solution. In both the simulated body fluids the wear behaviour of the samples heat treated at different solution treatment temperatures shows an almost similar trend with furnace cooled and aged samples showing the lowest wear rate in most of the cases.

The coefficient of friction of the heat treated TZNB alloy (measured in the steady temperature region) varied from 0.24 to 0.40 in dry condition, 0.45–0.50 in Hank's solution and 0.41–0.49 in bovine serum. In wet condition, compared with TZN alloy [20], TZNB alloy showed an overall increase in the coefficient of friction (Figs. 9b, 10b and 11b). Like in TZN alloy, the presence of lubricant during wet wear tests prevented any significant temperature rise at the contact point between the TZNB alloy and the counterface material.

The counterface material used in these experiments was high chromium steel which is much harder than TZNB alloys. Pull-out of hard TiB particles is expected to takes place when TZNB samples are rubbed against this hard surface in dry condition. This results in three-body abrasive wear. The hard TiB particles get entrapped between the TZNB pin and steel disc and cause the material of the pin to wear off. This is the reason for faster wear of TZNB samples. In the case of TZNB sample deformed at 800 °C and solution treated at the same temperature followed by water quenching and aging, an increase in wear resistance can be attributed to the fine precipitation of α along the pre-existing martensite plates.

The increase in wear rate in Hank's solution can be attributed to the influence of corrosion on the surface of the titanium alloy [20] and it is further accelerated in the presence of TiB particles. The corrosive wear is more detrimental for mixed phase alloys than for single-phase alloys because in a mixed phase alloys a number of local galvanic cells

Fig. 11. Wear behaviour of TZNB alloy in bovine serum. Samples were deformed at 800 °C or 650 °C followed by heat treatment under different conditions: (a) wear rate and (b) coefficient of friction.

Fig. 12. Hardness vs. wear rate of the heat treated TZNB alloy deformed at 800 °C or 650 °C followed by heat treatment under different conditions: (a) dry condition (b) Hank's solution and (c) bovine serum.
form which accelerates the corrosion \[40\]. In the case of furnace cooled, air cooled or aged TZNB samples solution treated at 800 °C, the microstructure consists of \(\alpha\), \(\beta\) and TiB phases. Results indicate that these TiB particles when present along with \(\alpha\) phase in \(\beta\) matrix increase the corrosion of the material \[21\]. Therefore, compared with TZN alloy, the TZNB alloy consisting of multiphase microstructure shows a significant increase in the wear rate in Hank's solution. On the other hand, the only difference in microstructure of TZN and TZNB alloys, when quenched from 800 °C, is the presence of TiB precipitates in the latter and hence presence of small amount of TiB and absence of any \(\alpha\) phase in the microstructure does not significantly affect the wear rate of TZNB alloy in Hank's solution. However, when TZNB samples were subjected to deformation at 800 °C or 650 °C and then air cooled or water quenched from a solution treatment temperature of 650 °C a substantial increase in wear rate in Hank's solution was observed when compared with TZNB sample water quenched from 800 °C. Air cooling from the solution treatment temperature of 650 °C led to the formation of finely dispersed microstructure consisting of \(\alpha\), \(\beta\) and TiB. On the other hand, in the case of sample water quenched from 650 °C, martensite does not form and the microstructure consists of \(\alpha\) and \(\beta\) phases in addition to TiB. Moreover, rapid cooling during water quenching prevents any growth of the \(\alpha\). Hence, the high wear loss of the air cooled and water quenched samples can be attributed to this finely distributed multiphase microstructure that increases the wear rate as discussed above. It can be recalled that the microstructure of the water quenched sample that was deformed and solution treated from 800 °C consisted of only martensite and TiB in \(\beta\) matrix and \(\alpha\) was not present. Hence compared with other water quenched samples, this sample showed higher wear resistance in Hank's solution. In Hank's solution, aging treatment improves the wear resistance of the TZNB samples water quenched from a solution treatment temperature of 650 °C. This can be attributed to decrease in \(\alpha/\beta\) interface area due to coarsening of the \(\alpha\) phase during aging.

All the TZNB samples subjected to different heat treatment conditions consisted of TiB particles and their wear behaviour in Hank's solution was found to depend mainly on the amount and morphology of the \(\alpha\) phase. Nevertheless, boron does affect the wear properties indirectly because it influences the growth and morphology of the \(\alpha\) phase. However, when TZNB is compared with TZN, TiB plays a significant role as described earlier because it makes the microstructure more heterogeneous by incorporating an additional phase in the form of TiB.

In bovine serum, the wear behaviour of the material is mainly influenced by the effect of protein layer on the contact surfaces \[23,24,26\]. It is believed that the protein attachment to the bearing surfaces is affected by the solid/lubricant interfacial energy which in turn is influenced by the characteristics of the material at the contact surface \[20\]. However, further study is needed to confirm it.

Like TZN alloy, TZNB alloy also showed no clear relationship between the hardness and wear resistance of the heat treated samples (Fig. 12), though the samples deformed and solution treated at 800 °C tended to show a small increase in wear rate with hardness.

The SEM micrographs of the wear surface of TZNB alloy in dry condition, in Hank's solution and in bovine serum are presented in Figs. 13–15 respectively. In dry condition, SEM study revealed deep parallel scars on the wear surface of the TZNB alloy (Fig. 13). This can be attributed to pull-out of hard TiB particles causing the three-body abrasive wear. In the case of Hank's solution or bovine serum, parallel scars with patches of surface deformation were seen (Figs. 14 and 15). The wear debris of the samples consisted of irregular shaped particles

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**Fig. 13.** SEM micrograph of the wear track of TZNB alloy in dry condition; samples deformed and solution treated for 1 h at 650 °C followed by (a) air cooling and (b) water quenching and aging.

**Fig. 14.** SEM micrograph of the wear track of TZNB alloy tested in Hank's solution; sample deformed and solution treated for 1 h at 650 °C followed by (a) air cooling and (b) water quenching and aging.
with very sharp edges (Fig. 16). The fragmented particles are relatively large and more elongated in Hank’s solution and bovine serum than in dry condition. This can be associated with the higher amount of wear loss in fluid media than in dry condition. The composition of the wear debris obtained after wear tests in all the three media (air, Hank’s solution and bovine serum) is presented in Table 1, which shows iron pick up from the counterface material by the wear debris during wear testing.

4. Summary and conclusions

- Addition of 0.5 wt.% B to TZN alloy resulted in the formation of dispersed precipitated particles of titanium boride (TiB). The majority of the boride precipitate particles were acicular (needle like) with lengths varying in the range of 5–10 µm with some particles being even larger than that.
- Boron had no appreciable effect on the overall microstructure of the TZN alloy samples that were deformed and solution treated at 800 °C. However, the aged sample showed some growth of the α phase. In the case of TZNB alloy solution treated at 650 °C after deformation at 800 °C or 650 °C, growth of the α phase was observed in the microstructure.
- In most of the cases, addition of boron to the TZN alloy did not improve the hardness.
- In the case of dry wear of TZNB samples, no significant variation of the wear rate with heat treatment was observed except for the samples aged after water quenching from a solution treatment temperature of 800 °C, which showed relatively high wear rate.
- Compared with the wear rate in dry condition, the wear rate in Hank’s solution of the all the TZNB samples increased substantially.

Table 1

<table>
<thead>
<tr>
<th>Wear test condition</th>
<th>Ti (wt%)</th>
<th>Zr (wt%)</th>
<th>Nb (wt%)</th>
<th>Fe (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>71.73</td>
<td>10.90</td>
<td>16.66</td>
<td>1.91</td>
</tr>
<tr>
<td>Hank’s solution</td>
<td>71.34</td>
<td>12.57</td>
<td>13.95</td>
<td>1.56</td>
</tr>
<tr>
<td>Bovine serum</td>
<td>71.93</td>
<td>12.81</td>
<td>13.86</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Boron content in the alloy cannot be measured by EDS.
The wear was most severe in bovine serum. In both the simulated body fluids the wear behaviour of the samples heat treated at different solution treatment temperatures showed an almost similar trend with furnace cooled and aged samples showing the lowest wear rate in most of the cases. In general, relatively rapid cooling after solution treatment (i.e. air cooling or water quenching) resulted in higher wear rate in wet condition.

- In dry condition, the dominating wear mechanism was micro-cutting. In Hank’s solution, rapid formation of a passive layer on the contact surface of the material and its subsequent removal during the next sliding contact played a major role during the wear process. In the case of bovine serum, the wear mechanism was mainly abrasive.

- Compared with TZN alloy, TZNB alloy exhibited an overall increase in the coefficient of friction.

- There was no clear relationship between the hardness and wear resistance of the heat treated TZNB samples.

- Boron containing TZNB alloy did not show any improvement in the wear resistance in all the media studied when compared with TZN alloy after same heat treatment.

**References**


