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# Microstructure, mechanical properties and electrochemical behavior of a novel biomedical titanium alloy subjected to thermo-mechanical processing including aging

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ABSTRACT

This paper presents the results of a study in which influence of different thermo-mechanical processing (TMP) parameters on the mechanical properties and electrochemical behavior of a new metastable β alloy Ti–20.6Nb–13.6Zr–0.5V (TNZV) was investigated. The TMP comprised of plastic deformation in β phase field (850 °C) followed by solution heat treatments at below β transus temperature (650 °C) and cooling at various rates in addition to aging. Depending upon the TMP conditions, a wide range of microstructures with varying spatial distributions and morphologies of equiaxed/elongated α, β phases were attained which allowed a wide range of mechanical and electrochemical properties to be achieved. The corrosion behavior of the alloy used in the present study was evaluated in a Ringer's solution at 37 °C using open circuit potential–time and potentiodynamic polarization measurements. The results of the study revealed that amongst different solution treated samples, water quenched (WQ) samples exhibited optimum results of elastic modulus, elongation, corrosion resistance as well as reasonable strength and hence it can be considered to be a potential candidate for biomedical applications.



## 1. Introduction

Multifunctional β-type Ti alloys which widely used in various biomedical applications have been developed all over the world. Recently, some new near β-type Ti alloys containing β-stabilizers such as Nb and Zr have attracted much special attention for orthopedic implants applications owing to their unique combination of better mechanical properties, low Young's modulus, superior biocorrosion resistance, nontoxicity against osteoblastic cells, no allergic problems, and excellent biocompatibility. The required mechanical properties in this kind of Ti alloys can be improved due to solid solution and second phase strengthening while preserving the light weight characteristics of Ti [1,2]. From crystallographic insight, the body centered cubic structure (bcc) of β phase shows higher symmetry as compared to the hexagonal closed packing (hcp) α phase resulting in an isotropic mechanical behavior. Moreover, it is found that their Young's modulus can be significantly reduced by adjusting the concentration of β stabilizing elements [3–5] which makes them appropriate for load bearing surgical implants. In addition, this type of Ti alloys exhibits extraordinary corrosion resistance in human body fluid. This behavior is due to the formation of a protective, hard and tightly adherent oxide film [6]. This oxide film offers chemical inertness to the Ti implants in human body fluid and guarantees its biocompatibility as a biomaterial. Therefore, Ti-based alloys with nontoxic and non-allergic elements such as Nb, Zr, and other elements have been widely used to design new β-type Ti alloys [7]. In this regard, the addition of Nb and Zr is preferable to develop absolutely safe Ti-based alloys for biomedical applications depending upon its ability to achieve biological passivity and capacity of reducing the elastic modulus [8].

In general, thermo-mechanical processing (TMP) is a metallurgical process that integrates work hardening and heat-treatment into a single process [9] plays a crucial role to produce a microstructure with outstanding properties in the materials [10–12]. The mechanical properties as well as corrosion behavior depend strongly on the alloy composition, processing history, heat treatment conditions which decide the varieties of microstructures. Near-β Ti alloys respond to thermal treatment and TMP and various microstructural constituents like the size, shape and

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the amount of the various phases can be modified by varying the TMP parameters. However, the influence of thermal treatment and TMP on microstructural features of as-cast Ti–Nb–Zr alloy system and in turn on its mechanical and electrochemical behavior is scarcely reported.

Nowadays, great efforts in terms of extensive work and focus are being dedicated by engineers and materials scientists in developing novel Ti alloys for biomedical applications with low Young's modulus and superior electrochemical behavior. In this study, titanium–niobium–zirconium based alloy containing small amounts of vanadium was investigated in order to evaluate its possible application as a biomedical material. Niobium, zirconium and vanadium, having a β-phase stabilizing effect for titanium materials, were chosen to control microstructure desirably. In spite of the fact V is associated with toxicity, the concentration used in this study is minimal. Microstructure control was carried out by performing hot working in β field and subsequently heat treatment in (α + β) field with different cooling rates. Finally, the relationship between thermo-mechanical processing, mechanical properties and corrosion behavior was explored and also discussed in detail.

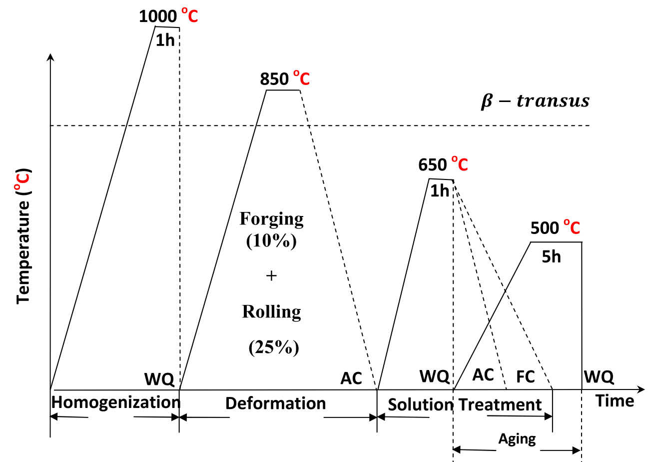


**Fig. 1.** Schematic diagram of the thermo-mechanical processing of TNZV alloy.

## 2. Material and methods

The alloy in the present investigation was cast using the facility available at DMRL, India with mixture of sponge Ti along with niobium powder and zirconium chips as raw materials. The Ti–20.6Nb–13.6Zr–0.5V (TNZV) alloy was prepared using the non-consumable vacuum arc melting technique and supplied in the form of 600 g pancakes. The pancakes were re-melted three times to ensure compositional homogeneity, so obtaining compact and homogenous ingots with neither weight loss nor oxidation. The composition of the alloy was analyzed and the same in wt% is given in Table 1.

The as-cast TNZV alloy was then heat-treated at 1000 °C for 1 h for homogenization, and water cooled. In order to determine the β transition temperature (β transus) of the newly developed TNZV alloy, differential scanning calorimeter (DSC) analyses have been performed under protective argon atmosphere, at a scanning rate of 10 °C/min, to the maximum temperature of 800 °C. The β transus of the alloy was measured to be 695 °C. Subsequently, the homogenized samples were given 10% reduction by forging at above the β transition temperature (850 °C) and directly subjected to 25% reduction by rolling at same temperature and were then air cooled to room temperature. After entire plastic deformation was accomplished, the alloy remained free from any of the metal working defects which indicated that the entire metal working process was performed successfully. The hot deformed TNZV samples were solution treated at 650 °C (below β transus) for 1 h in a dynamic argon atmosphere; this was followed by furnace cooling (FC), air cooling (AC), or water quenching (WQ). Aging treatment was done only on the WQ samples at 500 °C for 5 h. The TMP route of TNZV alloy is shown schematically in Fig. 1.

The composition of the major and trace elements was determined using X-Ray Fluorescent (XRF) Spectrometer (*Oxford-X Srata*, model: *ISIS 1559*). Microstructure analysis of the heat treated samples was carried out using an optical microscope and field emission scanning electron microscope (*FE-SEM*, *NOVA NANO SEM 450 FEI*, *Netherlands*) at 2 kV. For this, the metallographic samples were prepared using standard techniques for Ti and its alloys [13]. The samples were ground to 1200 grit with silicon carbide (SiC), followed by final polishing to a mirror finish using 0.5 μm diamond paste. The metallographically polished samples were etched with Kroll's reagent (*10 vol% HF and 5 vol%* $HNO_3$ *in water*). Room temperature X-ray diffraction analysis was carried out using an X-ray Diffractometer, *Philips*, *Holland*, *PW 1830* with Cu Kα radiation (wavelength 1.54056 Å) at an accelerating voltage of 40 kV and a current of 30 mA.

Vickers micro-hardness measurements were performed using a computer controlled precision micro-hardness tester (model: *MicroWhizHard;* make: *Mitutoyo*, *Japan*) with an indentation load of 300 gf and a dwell time of 5 s for each of the indents. Ten indentations were taken for each specimen and the average values were considered. Hardness measurements were carried out on the samples finished using 0.5 μm diamond paste.

Tensile testing was performed as per ASTM E8 M to determine the ultimate tensile strength (UTS), 0.2% off-set yield strength (YS) and elongation (e%) using a conventional tensile testing unit (*Computerized FIE Make Universal Testing Machine*, Model *UTE-60*), with a constant cross-head speed of 1 mm/min in air at room temperature. Dog-bone-shaped tensile specimens with dimensions: 10 mm width, 4 mm in thickness and a gage length of 25 mm were precisely machined using Wire Electrical Discharge Machine (*Wire-EDM*). After machining, tensile specimens were polished using SiC waterproof papers of up to #2500 grit and the gage length of the specimens was mechanically polished using a diamond paste with a particle size 0.5 μm.

**Table 1**
The chemical composition (wt%) of TNZV alloy used in this study.

| Ti (wt%) | Nb (wt%) | Zr (wt%) | V (wt%) | Fe (wt%) |
|---|---|---|---|---|
| Balance | 20.6 | 13.6 | 0.5 | 0.14 |

The corrosion behavior of the TNZV alloy was studied using potentiostat comprising of three-electrode cell with an Ag/AgCl (KCl saturated) as the reference electrode (all the potential measurements were made with reference to it) and a platinum foil as the counter electrode (cathode). The test specimens with dimensions (10 mm × 10 mm × 2 mm) served as a working electrode (anode). Anodic polarization was carried out with a corrosion measuring system (model: *WPG100e*, *Korea*) which was computer interfaced through relevant software named *Sequencer* version 5. The open circuit potential (OCP) and passive current density were used as the criterion for evaluating the corrosion characteristics of the thermo-mechanically processed Ti alloy. The surface area exposed to the electrolyte was 0.126 $cm^2$. For each experiment, the specimens were prepared by sequential grinding with waterproof emery paper up to 2000 grit SiC, followed by polishing with alumina of 0.5 μm for getting high mirror surface finish and then cleaning in an ultrasonic bath for three times. Freshly prepared Ringer's solution was used as the electrolyte for each experiment to simulate physiological conditions representative of what a biomedical component would experience [14]. The solution had the following chemical composition dissolved in one liter of distilled water: *9.00 g NaCl*, *0.43 g KCl*, *0.20 g* $NaHCO_3$ *and 0.24 g* $CaCl_2$. The pH of the solution was maintained at 7.4. The solution was naturally aerated and kept at 37 ± 1 °C which is equivalent to human body temperature throughout the tests. Upon immersion of the specimens into the electrolyte, the open-circuit potential (OCP) was measured as a function of time, until the stable value was reached. Consequently, corrosion potential ($E_{corr}$) and passive current density ($I_{corr}$) of the alloy were determined from the potential vs. current density polarization curve. The polarization curves were obtained with a scan rate of 0.166 mV/s in the range from −750 to 2500 mV(Ag/AgCl). The polarization tests were repeated at least three times for each specimen. The corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) were determined from the registered curves by the extrapolation method.

## 3. Results and discussion

### 3.1. Microstructure and XRD analysis

The "metastable – β – alloy" used in the present research was subjected to thermo-mechanical processing. The optical microscopy (OM) and scanning electron microscopy (SEM) performed on the as cast alloy samples showed the presence of fine needle like α phase (acicular α) in former β-phase matrix with segregation of α phase on grain boundaries (Fig. 2). For each former β-grain, twelve different crystal orientations of the α precipitates (variants) are available according to the Burgers relationship [15], which links particular crystal directions and planes of both phases:

$$\langle 1\,1\,1\rangle_{\beta}//\langle 1\,1\,2\,0\rangle_{\alpha},\ (1\,1\,0)_{\beta}//(0\,0\,0\,1)_{\alpha}$$