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Influence of boron nitride reinforcement to improve high temperature oxidation resistance of titanium

Jose D. Avila, Amit Bandyopadhyay*

W. M. Keck Biomedical Materials Research Lab, School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA.

Abstract

Influence of boron nitride (BN) addition in commercially pure titanium (Cp-Ti) was characterized for their microstructural variation, hardness and oxidation kinetics. Feedstock powders Cp-Ti with 3 wt.% BN (3BN) and 6 wt.% BN (6BN) were prepared by roller mill followed by additive manufacturing using laser engineered net shaping (LENSTM). Rate of oxidation was measured from thermogravimetric analysis (TGA) at 1000°C for 50 h. Average instantaneous parabolic constants (k_p) for Cp-Ti, 3BN and 6BN were 41.2 ± 12.0 , 28.6 ± 2.8 and 18.2 ± 9.2 $\text{mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1}$, respectively. Cp-Ti displayed acicular α -Ti microstructure. After TGA, large equiaxed grains along with TiO_2 formation at the grain boundaries was observed, which increased the hardness. With BN addition, plate-like TiN and needle-like TiB secondary phases were also observed. Hardness for Cp-Ti, 3BN and 6BN were 256.9, 424.0 and 548.3 $\text{HV}_{0.2}$, respectively. Overall, a small addition of BN was effective in improving the oxidation resistance of Cp-Ti.

Keywords

Laser engineered net shaping; oxidation; titanium; boron nitride; titanium nitride; titanium boride

1.0 Introduction

Titanium (Ti) is a silver color transition metal with characteristics that make it attractive for widespread use in automotive, chemical, medical and aerospace applications; characteristics such as high corrosion resistance, high strength-to-weight ratio, excellent fatigue resistance and a relatively high melting point ($\sim 1,650$ °C) [1]–[5]. Specifically, for elevated temperature applications, Ti's low thermal conductivity, high specific strength, and low thermal expansion ($8.6 \mu\text{m} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) are key features. Additionally, Ti always has an outer oxide layer, titanium dioxide (TiO_2), which is typically 4–5 nm in thickness [6]. The continuous and dense TiO_2 passivation layer restricts the diffusion of oxygen into the bulk material. In this case, parabolic oxidation kinetics are observed up to 600 °C [7]. The assumption with parabolic oxidation kinetics is that diffusion of oxygen through the coherent oxide layer is the rate limiting step [8]. At higher temperatures (>600 °C), deterioration of the passivation layer occurs resulting in linear oxidation kinetics with continued and uncontrolled reaction

*Corresponding author: amitband@wsu.edu.

or absorption of oxygen. Linear oxidation kinetics are a direct result of a cracked or porous oxide layer where transport of ions occurs faster than the chemical reaction [8].

Several surface treatment techniques have been implemented to increase Ti's oxidation resistance. Such techniques can be based on either chemical or mechanical modifications. Examples of chemical modifications comprise of cementation coatings [9], physical vapor deposition (PVD) of ceramic coatings [10] and ion implantation [11]. Mechanical modifications include shot-peening to increase oxidation resistance and fatigue performance of alloys [12], [13]. Addition of ceramic particles into a metal matrix to form a metal-matrix composite (MMC) have also been attempted to improve oxidation resistance. Examples of some of the MMCs produced by LENSTM include vanadium carbide reinforced stainless steel [14], niobium carbide reinforced stainless steel [15] and calcium phosphate reinforced Ti6Al4V [16]. Improvements in mechanical properties and oxidation resistance of LENSTM fabricated MMC's have also been achieved through *in situ* ZrB₂ formation in Zr matrix [17] and TiB reinforcement in Ti matrix [18]. Previous work has shown that small reinforcements improve the mechanical and thermal stability of Ti-MMCs [19]. In general, it was reported that the reason for improved mechanical properties and oxidation resistance was due to impregnation or *in situ* formation of harder ceramic particles in the bulk material, which exhibited higher thermal stability and sound metallurgical bonding between the matrix and the reinforcement materials [14]–[18].

BN by itself exhibits poor oxidation resistance, low hardness and poor mechanical strength [20]. However, its reaction with Cp-Ti is postulated to form TiN, TiB and TiB₂, which are refractory materials and exhibit excellent mechanical as well as thermal stability. When BN and Cp-Ti reacts at 927 °C in an oxidizing environment, the following reactions would result [1]:

with the introduction of BN [21]:

with the formed products having heats of formation of: – 70.1 for TiN, – 28.0 for TiB, – 53.0 for TiB₂ and – 211.0 kcal·mol^{–1} for TiO₂ [22]. It should be noted that the order of products formation during reaction of Ti and BN thermochemically favors the formation of TiB₂; this is due to heat of formation of TiB₂ being more negative than the heat of formation for TiB. However, the presence of TiB₂ in high Ti concentration will favor Reaction 4 due to the small heat of formation [23]; more specifically, TiB formation will occur if the concentration of B is <18–18.5% in the reaction zone [24]. To reiterate, in low Ti and high

BN concentrations, TiB_2 should be expected [25] as is the case with initial reaction of B with Ti around BN particles. However, in the case of high concentration of Ti, formation of TiB is more favorable than TiB_2 following Reaction 4 [26].

To finalize, even if initially TiB_2 is formed due to initial abundance of BN, only TiB formation should be expected via solid-state reaction in post-oxidation samples as diffusion will occur in the elevated temperature environment and subsequently reduce B concentration in the localized reaction zone [27].

In the present study, it was hypothesized that addition of BN to Cp-Ti would form *in situ* TiN, TiB and enhance the oxidation resistance of the composite. The aim of this work was to understand how BN introduction into Ti influences oxidation resistance, microstructure and hardness of the formed Ti-MMC as a function of increased BN concentration and oxidation time. Ti-MMC samples were prepared for oxidation studies at elevated temperatures where oxide layer adhesion was not expected but the oxidation kinetics were reduced due to modified chemical composition of the bulk material. In this work, Cp-Ti and BN powders were used as starting material for LENSTM based additive manufacturing. The objective of this research was to increase Cp-Ti's oxidation resistance by single-process shape fabrication and *in situ* reinforcement formation using LENSTM.

2.0 Results

2.1 Oxidation

Early-stage and steady-state oxidation rates were compared for Cp-Ti, 3BN and 6BN from the mass percent change curves with respect to time. The following time intervals were used: early-stage (1.6–3.2 h) and steady-state (25–50 h). Isothermal temperature was attained after 1.6 h, therefore early-stage characterization began at this time with the obtained results shown in Table I. Linear and non-linear regression were performed as to attain a coefficient of determination (R^2) as close to '1' from experimentally collected data. For this work, modeling with respect to traditionally known and established oxidation laws was also done, typically performed using mass gain over surface area with respect to time curves, as shown in Figure 1. The following general oxidation laws were used. Specifically, for non-linear oxidation kinetics, the equation is [28]:

$$\frac{\Delta m}{S} = (kt)^{\frac{1}{n}} \quad (5)$$

where, m is the mass change due to oxidation, S is the exposed surface area, k is the diffusion rate constant, n is the degree index of the oxidation law and t is time in hours. A value of $n = 2$ in this equation would account for parabolic kinetics, which is indicative of a protective barrier [29]. For linear oxidation kinetics, the equation is [30]:

$$\frac{\Delta m}{S} = k_l t \quad (6)$$

where k_l is a linear oxidation constant as discussed by the two aforementioned references [29, 30].

To further understand the evolution of the oxidation rate modeling under differentiated parabolic condition is done, as discussed in [31], [32]. In this approach, the instantaneous parabolic constant (k_p) value gives a better representation of the evolution of the oxidation rate for the entirety of the test. To achieve this, a value of 2 is used for n and Equation 5 can be rewritten as:

$$\left(\frac{\Delta m}{S}\right)^2 = (k_p t) \quad (7)$$

In this form, parabolic kinetics are assumed. Following with differentiation of Equation 7 with respect to time, k_p may be isolated and Equation 7 may be rewritten as:

$$\frac{d\left(\frac{\Delta m}{S}\right)^2}{dt} = k_p \quad (8)$$

Early-stage and long-term relative mass% oxidation rates were calculated for Cp-Ti, 3BN and 6BN for TGA samples, and presented in Table I. Cp-Ti displayed early-stage oxidation rate of $6.07 \times 10^{-2} \text{ mass\%} \cdot \text{min}^{-1}$. Oxidation rate for 3BN and 6BN compositions decreased to 1.92×10^{-2} and $1.42 \times 10^{-2} \text{ mass\%} \cdot \text{min}^{-1}$, respectively. No significant difference is observed in the long-term oxidation rates for Cp-Ti and 3BN compositions, but a decrease of ~50% is observed for the 6BN composition. To further analyze the thermogravimetric (TG) data for the oxidized samples, traditionally reported oxidation models using Equations 5 and 6 were done. Figure 1 displays the TG curves for the three compositions in the mass gain with respect-to-time format. A power fit curve is displayed in Figure 1a following Equation 5, for the 3BN composition. The remaining two TG curves presented R^2 values below 0.98 and therefore power regression of data as a whole was not implemented. Instead TG curves for Cp-Ti and 6BN compositions were segregated into two regions: linear (Figure 1b) and non-linear (Figure 1c) using Equations 6 and 5, respectively. Linear constant (k_l), diffusion rate constant (k) and index of oxidation law (n) are presented in Table I. The general trend is a reduction in k_l and k , with the exception of 3BN, which was not segregated. To further analyze the evolution of k during testing, instantaneous parabolic constant (k_p) curves were derived using Equation 8 and presented in Figure 3. More fluctuation Cp-Ti's k_p value is observed when compared to 6BN composition, with Cp-Ti having a higher k_p value throughout testing, while composition 3BN displaying the least fluctuation. The average k_p value for Cp-Ti, 3BN and 6BN from 10 h to 50 h are approximately 41.2 ± 12.0 , 28.6 ± 2.8 and $18.2 \pm 9.2 \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1}$, respectively. Correlating to change in mass, 3BN and 6BN

displayed a reduction of 22.3% and 35.3% when compared to Cp-Ti, respectively. To generalize, a decrease in k_p value is consistent with increased BN concentration in the samples.

2.2 Phase Analysis

Figure 2 displays the X-ray diffraction (XRD) spectrums for LENSTM processed Cp-Ti, 3BN and 6BN samples. Cp-Ti displays only α -Ti phase. With the addition of BN, composition 3BN displays the formation of osbornite (TiN), metastable $\text{TiN}_{0.176}$, TiB and unreacted BN. Composition 6BN exhibits a similar spectrum to that of 3BN but with a significant increase in the TiN peaks.

2.3 Microstructure

LENSTM processed pre-TGA Cp-Ti composition displayed typical acicular α -Ti or also referred to as α' -Ti microstructure as seen in Figure 4a. After oxidation, the needle-like microstructure was changed and larger equiaxed grains were observed, as shown in Figure 4d. Along with the increased grain size, precipitates along the grain boundaries were observed and increased in size with increased oxidation time, Figure 4g.

LENSTM processed pre-TGA 3BN's microstructure was not of α' -Ti but involved two different morphologies of secondary phases, as seen in the inset of Figure 4b and Figure 5a. The small needle-like structures are TiB needles, while the plate-like regions are TiN within the Ti matrix. A similar microstructure is observed in the 6BN composition, however TiB needlelike microstructure and TiN regions are larger, shown in Figure 4c inset and Figure 5b. After 50 h TGA, TiB in the 3BN composition is observed to evolve into coarser needle-like microstructure. For both 3BN and 6BN after 50 h TGA, TiN plate-like microstructure is absent as can be seen in Figure 4h and inset in 4i or at higher magnification in Figure 5c and 5d.

2.4 Hardness

Vickers hardness values for Cp-Ti, 3BN and 6BN at varying oxidation times are shown in Figure 6. As processed LENSTM Cp-Ti sample had the lowest hardness at $256.9 \pm 7.7 \text{ HV}_{0.2}$, which increased with oxidation time to $424.0 \pm 33.6 \text{ HV}_{0.2}$ and $548.3 \pm 49.7 \text{ HV}_{0.2}$ for 25 h and 50 h testing, respectively. As processed 3BN and 6BN LENSTM samples hardness were $538.1 \pm 19.1 \text{ HV}_{0.2}$ and $584.7 \pm 27.0 \text{ HV}_{0.2}$, respectively. After 25 h TGA, 3BN and 6BN samples hardness increased to $714.2 \pm 36.6 \text{ HV}_{0.2}$ and $717.9 \pm 20.0 \text{ HV}_{0.2}$, respectively. No significant increase in hardness amongst 50 h TGA 3BN and 6BN samples was observed – where 3BN and 6BN samples exhibited a hardness of $773.4 \pm 50.9 \text{ HV}_{0.2}$ and $759.2 \pm 27.6 \text{ HV}_{0.2}$, respectively.

3.0 Discussion

3.1 Oxidation

Reported literature on Ti's oxidation mechanisms have shown that four rate laws can be applied within the temperature range of 300–1000 °C. The reported rate laws are: logarithmic, cubic, parabolic, and parabolic + linear [8]. A logarithmic rate law is indicative

of oxide film formation and is reported to follow a Mott-type mechanism. A cubic rate law is associated with the diffusion of oxygen into titanium. A parabolic rate law follows the assumption that diffusion of oxygen through the oxide layer is the rate limiting step and follows the Wagner high-temperature mechanism. Lastly, a linear rate law results when cracks in the oxide layer occur and the rate limiting step is a phase boundary reaction [7], [8]. In the process of rendering an oxidation kinetic law for collected data, parameters that can add to the complexity of properly modeling the data are testing temperature, oxygen concentration, oxygen pressure, residual stresses in the material, sample composition, and gas composition. Although, current literature has shown that the most significant contributor on oxidation kinetics is temperature [6]. To decrease complexity, segregating experimental curves into more than one or two-time intervals is not uncommon and allows for improved modeling of the oxidation kinetic stages. For example, LENSTM processed 50 h TGA Cp-Ti and 6BN collected data had to be segregated into a linear region and a power law region, displayed in Figure 1b and 1c. Segregating the collected data allowed for improved modeling as a coefficient of determination value closer to '1' was achieved.

Oxidation rates in the units of $\text{mass}\% \cdot \text{min}^{-1}$ were calculated to understand compositional variation effects on oxidation resistance. The values are presented in Table I. When 3BN and 6BN samples are compared to Cp-Ti, a reduction in oxidation rate can be seen by a factor of 3 and 4, respectively. Long-term or steady-state oxidation rate difference is undisguisable for Cp-Ti and 3BN compositions, but a reduction of 50% is observed for 6BN; the reason for similar steady-state oxidation rate for Cp-Ti and 3BN is due to lower BN presence and oxygen saturated Ti matrix. The reduction in oxidation rate for 6BN sample is due to higher BN content.

Using Equation 5, LENSTM processed 50 h TGA 3BN sample was the only composition to produce an acceptable R^2 value for the entirety of the test. Table I displays the oxidation constants and degree index values of the oxidation laws. The linear oxidation law was used for LENSTM processed 50 h TGA Cp-Ti and 6BN samples at early-stages of oxidation and produced constant values of 6.29 and 1.7. Linear oxidation behavior occurs due to non-restrictive diffusion of oxygen and uncontrolled oxidation kinetics. The oxidation reactions are exothermic and cause an increase in surface temperature and an increase in the reaction kinetics [29]. Self-propagating high temperature synthesis has been reported for such exothermic reactions which can add further to the observed linear kinetics [25]. In the case of Cp-Ti, the abundance of Ti and spallation of the TiO_2 passive layer, observed in Figure 7, can account for the linear oxidation kinetics. In the case of 6BN unreacted BN with Ti, as seen in Figure 4b, accounts for the linear kinetics; this is due to BN's poor oxidation resistance at elevated temperature and initial self-propagating characteristics.

In modeling non-linear oxidation kinetics with Equation 5, diffusion oxidation rates are 9.28, 3.14 and 4.81 for Cp-Ti, 3BN and 6BN, respectively, Table I. The trend is a decrease in oxidation rate as BN percent is increased. The exception is 3BN, but this is the accepted variation for having the general oxidation power law fit the entirety of the collected data. In discussing the degree index of the oxidation law (n), it was previously stated that a value of '2' accounts for parabolic oxidation rate kinetics and is indicative of a protective barrier.

6BN gives a degree index value closest to '2' and therefore exhibits such protective barrier kinetics.

Figure 3 displays k_p values for Cp-Ti, 3BN and 6BN during the 50 h TGA test. Presenting the data in this fashion, it can be easily seen why only 3BN produced an R^2 value of over 0.98 for the power law; 3BN's k_p value remained consistent throughout testing. Cp-Ti displayed the greatest instantaneous k_p value at early and long-term testing. This can be due to oxygen saturating the Ti matrix, as is the case in temperatures exceeding 800 °C [8]. Also, fluctuations can be interpreted as barrier formation and subsequent cracking and spallation. Upon the addition of BN, 3BN displayed a drop in the k_p value. For the 6BN, fluctuation was greater but after 30 h remained below 3BN. The reactions occurring are exothermic. The combination of small specific heat and large heat of formation classify the reactions as self-propagating high-temperature synthesis [33].

3.2 Phase analysis

For as processed 3BN and 6BN samples, $TiN_{0.176}$, TiN and TiB formation was observed, as seen in Figure 2. TiB_2 could not be detected due to low percent of BN, favoring Reaction 2 over Reaction 3. Observed amongst 3BN and 6BN is meta-stable $TiN_{0.176}$. The high energy density combined with the fast cooling rates possible with LENSTM processing appeared to have 'locked-in' this metastable N rich phase. Proximity of this phase can be argued to exist at the TiN plate-like microstructure observed in Figure 5a. The fast cooling rates can also account for the incomplete reaction of BN particles, similar results have been reported for Ti64 related work [34], [35].

3.3 Microstructure

Microstructure as a function of oxidation time—Acid etched SEM micrographs of LENSTM processed Cp-Ti sample (Figure 4a) revealed acicular α -Ti microstructure. Fast cooling rates arise from low laser residence time, quenching by the substrate and laser scan speed when producing samples via any directed energy laser processing method [28], [36], [37]. LENSTM fabrication has been reported to exhibit cooling rates on the order of 10^3 - 10^5 K·s⁻¹ [38]. Fast cooling rates favor finer needle-like microstructure i.e., analogous to the martensitic microstructure of many metals when quenched [28], [37], [39]–[41]. This occurs because high cooling rates increase the nucleation rate of crystals, which in turn results in a finer dendritic structure. With respect to oxidation time, following the order of Figure 4a→4d→4g, precipitates are observed in Cp-Ti with increasing testing time when isothermally held at 1000°C. These TiO_2 precipitates formed at the grain boundaries due to oxygen rich environment [8]. Moreover, β -Ti is the phase present at the 1000 °C testing temperature and would thus allow for the ease of oxygen diffusion. An additional reason for unrestricted oxygen diffusion into the bulk material is the lack of a continuous passive TiO_2 layer at the surface, observable in Figure 7. Additionally, Ti grain size is observed to increase for Cp-Ti as testing time is increased; an expected observation as the elevated temperature is held isothermally for an extended amount of time and would allow grain growth to occur.

Microstructure as a function of BN concentration—With respect to increasing BN wt.% (Figure 4a-4c), the near complete loss of visible acicular α -Ti is observed. It can be argued that the lack of observable acicular α -Ti can be due to the change in Ti matrix composition such as B or N diffusion into the matrix. It may also be stated that the lack of acicular α -Ti microstructure is due to decreased cooling rates. Decreased cooling rates can occur due to the presence of BN and the formation of secondary phases of TiN and TiB, observed in Figure 4b and 4c or in Figure 5a and 5b. The three refractory materials have higher melting points and retain heat energy more readily when compared to Ti. Also, considering that TiN and TiB formation reactions are exothermic, heat energy would be of abundance and allow for overall heat retention in the material. Figure 4b of the 3BN composition displays a random oriented needle-like structure and plate-like microstructure morphology. The small needle-like structures are of TiB, and have been reported in previous work [24], [36], [42]. TiB needles can be fine and coarse, where it has been reported that coarse needles can either be hollow [43] or be of a Ti core [44]. The needle-like growth is in the [10] direction, which occurs because it is the fastest growth direction [24]; this combined with being bound by slower growing transverse planes [45] allows the TiB to grow as needles. It has also been reported that stacking disorder in the needle axis direction occurs and accounts for their lamellar structure [44]. The larger plate-like regions are TiN [36], [42] which was further verified by XRD analysis. An increase in plate size and coarsening of TiB needles are observed with increased BN wt.%, as seen from Figure 4b to 4c, and Figure 5a to 5b. The reason for increased geometric size with increased BN presence is due to the peak melt pool temperature increasing and allowing for increased diffusion, reaction and formation of larger TiN plates and coarser TiB needles [36]. Peak melt pool temperature increase with increased BN presence because BN has higher laser absorption coefficient than Ti [42]. TiB needles are seen to form around the TiN plate-like microstructure, as seen in Figure 5a. The reason for this networked microstructure is due to the diffusion of nitrogen into Ti during the interaction of BN and Ti. Boron having a higher atomic radius will exhibit a lower relative diffusivity in Ti matrix when compared to N, hence would increase the B concentration in the surrounding area while N diffuses away from the BN particles and nucleates as TiN in the core region. Similar TiB networked structure has also been reported in Ti-6Al-4V/TiB₂ composites after hot pressing treatment [46]. The increased laser absorption coefficient pertinent to BN allowed for increased heat retention upon LENSTM processing. Thus, allowing for the increased exothermic reactions of BN with Ti to occur and further increasing overall material heat retention. As a result, available Ti to react with oxygen was reduced.

Microstructure as a function of oxidation time and BN presence—As oxidation time was increased for 3BN sample, the fine needle-like TiB structure was observed to coarsen. This can be observed following Figure 4b→4e→4h and additionally in Figure 5a→5c, which can be due to the decomposition of unreacted BN. The 6BN composition, Figure 5b, needle-like TiB structure appears to have remained the same in size, that is Figure 5b→5d. This could indicate a maximum needle size was achieved within the 6BN composition. Apparent across both TGA tested BN samples is the visible loss of the TiN plate-like phase. Reported literature has discussed that N in TiN can escape into the gas

phase when exposed to 650 °C for 16 h [25]. Favored formation of TiO₂ and N₂ occurs – the reaction would be as follows [47]:

But, Reaction 9 is limited to occurring at elevated temperatures (>600 °C), which is not the case for the formation of TiO₂. Considering that it is a well-known fact that even at room temperature Ti self-passivates. Ultra-high resolution (UHR) through lens detector (TLD) SEM micrographs of 25 h TGA tested samples are displayed in Figure 9. A web-like intragranular microstructure is evident in the Ti matrix. It is believed that this secondary phase is of TiO₂ formation, Equation 9. By further evaluation of Figure 8 – N mapping, no apparent difference is observed in Cp-Ti and 6BN composition. Confirming there is no difference in N presence among the samples. N did indeed escape to the gas phase as the 6BN composition doesn't show an increase in N presence; this phenomenon analogous with the TiB₂ and TiB reaction order. Initial formation of TiN occurs due to the thermal energy associated with LENSTM processing and inert or oxygen deprived controlled environment. But, during TGA testing under an oxidative environment TiN degraded to TiO₂ and N₂, per Equation 9.

To finalize, smaller grain size is observed in the 50 h TGA 3BN (Figure 4h) and 6BN (Figure 4i) when compared to Cp-Ti (Figure 4g). A proposed reason for this is due to the insolubility of TiB into the Ti matrix, allowing for a higher concentration at grain boundaries that prevent grain growth via Zener pinning. An addition, grain refinement can also be due to implementation of elements into the Ti matrix with high growth restriction factors (GRF). For comparison, elements such as vanadium and aluminum, in Ti6Al4V alloy, have been given a GRF value of '0', or no significant influence on grain restriction. While silicon's GRF is 18.7 and B's GRF is reported to be 60 [48], [49]. The reported GRF associated with B could have had an influence in the observed smaller grains of Ti in 50 h TGA 3BN and 6BN samples.

3.4 Hardness

Hardness for Cp-Ti was observed to increase with oxidation time, shown in Figure 6. Oxygen is highly soluble in Ti and faster diffusion is reported to occur in β-Ti. Observed increase in hardness for Cp-Ti can be primarily due to the oxygen enriched Ti matrix. The oxygen saturated Ti is referred to as α-case Ti and is a direct result of interstitial diffusion of oxygen into the Ti lattice producing lattice distortion [7], and resulting in increased hardness. The enriched oxygen in Ti also allows for decreased oxidation kinetics, as observed in Figure 3 after 10 h. Both 3BN and 6BN compositions hardness increased due to the formation of TiN and TiB. With increased oxidation time, an increase in hardness was observed for both BN samples. It can be argued that the noticeable increase in hardness for LENSTM processed 3BN from 0 h to the 25 h oxidation is due to coarsening of TiB needles. While small grain size and intragranular precipitation, Figure 9, are also the reasons for increase in hardness for both 3BN and 6BN samples.

4.0 Conclusions

The objective of this research was to increase Cp-Ti's oxidation resistance by addition of BN and processing via LENS™ based additive manufacturing. Feedstock powders of 3 and 6 wt. % boron nitride in titanium matrix were prepared by roller mill. It was found that the oxidation resistance increased as the parabolic constant decreased by 55.8%, and the hardness increased by ~ 2.2 fold due to the addition of BN in Cp-Ti. Additionally, TiN and TiB formed *in situ* during LENS™ processing. After TGA, it was found that hardness increased across all three compositions. Hardness for the Cp-Ti increased due the formation of α -case Ti and TiO₂ nucleation at the grain boundary. Hardness increased for TGA tested 3BN and 6BN samples due to TiB needle-like microstructure coarsening and finer grain size because of Zener pinning. Overall, small addition of BN into Cp-Ti increased the oxidation resistance through microstructural modification, and *in situ* hard ceramic phase formation.

5.0 Materials and methods

5.1 Sample fabrication

Gas atomized Cp-Ti powder (Crucible Research, Pittsburgh, PA, titanium purity 99.998%) and hexagonal BN (99.99% pure, particle size: – 200 mesh ($\sim 74 \mu\text{m}$), Momen Performance Materials) powders were sieved to a particle size distribution of 49 to 145 μm . BN powder was the exception as its particle size range was of 49 to 74 μm . Powders were then mixed to attain two-powder mixtures of Cp-Ti + 3 wt.% BN and Cp-Ti + 6 wt.% BN. A maximum of 6 wt.% of BN was chosen for the study to show the proof of concept as previous LENS™ work showed desirable flowability at 5 wt.% BN in SS316 [27]. Feedstock powders of 3 wt.% BN and 6 wt.% BN were mixed using a roller mill at 40 rpm for 1 h in Nalgene plastic bottle having a diameter of 63.5 mm to ensure a homogeneous mixture. During milling process, no milling balls, binders or other additives were used. The prepared mixtures initialisms are designated as Cp-Ti, 3BN and 6BN corresponding to pure Cp-Ti powder, Cp-Ti + 3 wt.% BN, and Cp-Ti + 6 wt.% BN, respectively. Following the milling process, samples of Cp-Ti, 3BN and 6BN were processed on a 4 mm thick Cp-Ti substrate using a commercial LENS™ 750 system (Optomec Inc. Albuquerque, NM) equipped with a 500 W continuous wave Nd:YAG laser beam [28], with argon as the delivery gas. Processing parameters for Cp-Ti were laser power (LP): 427 W, powder feed rate (PFR): 200 $\text{mg}\cdot\text{s}^{-1}$, hatch scan velocity (HSV): 12.7 $\text{mm}\cdot\text{s}^{-1}$ and contour scan velocity (CSV): 12.7 $\text{mm}\cdot\text{s}^{-1}$. Parameters for 3BN were LP: 475 W, PFR: 233 $\text{mg}\cdot\text{s}^{-1}$, HSV: 12.7 $\text{mm}\cdot\text{s}^{-1}$ and CSV: 10.6 $\text{mm}\cdot\text{s}^{-1}$. Parameters for 6BN were LP: 500 W, PFR: 233 $\text{mg}\cdot\text{s}^{-1}$, HSV: 12.7 $\text{mm}\cdot\text{s}^{-1}$ and CSV: 10.6 $\text{mm}\cdot\text{s}^{-1}$. Closed-lid crucibles used for the integrated scale could only accommodate at most a sample size of 2 mm. Therefore, fabricated samples were cut into 2 mm cubes by waterjet. Cut samples were ultrasonically cleaned with 200 proof ethanol and allowed to dry before testing.

5.2 Thermogravimetric analysis (TGA)

TGA measurements for the LENS™ processed samples were performed using a Netsch STA 409 PC Luxx unit. For TGA measurement, the sample was loaded in an alumina crucible and covered with the lid having a hole at its center, with the sample weighed by internal unit

scale under gas delivery; this was followed by heating the sample from room temperature to 1000°C at 10°C·min⁻¹, and isothermally held for 25 h and 50 h, while weight change was measured with respect to time. Thermogravimetric measurement was completed by cooling to room temperature at 40°C min⁻¹. During measurement, compressed air at flow rate of 40 ml·min⁻¹ was supplied. The measurements were performed for Cp-Ti, 3BN and 6BN LENSTM processed samples with the obtained thermograms being used to establish oxidation kinetics.

5.3 Phase Analysis

Phase analysis for the LENSTM processed samples was performed using a PANalytical X'pert Pro MPD X-ray diffraction set-up (Royston, United Kingdom) with a Cu-K α radiation (1.54 Å) at 45 keV and 40 mA, scanning from 2 θ values of 30 to 80 degrees at a step size of 0.05 degree and a dwell time of 6 s. Obtained diffraction peaks for α -Ti, cubic-TiN, orthorhombic-TiB and hexagonal-BN for LENSTM produced samples were matched using reference cards from The Centre of Diffraction Data (ICDD). Alpha-Ti, cubic-TiN, orthorhombic-TiB and hexagonal-BN phases were referenced to ICDD cards: 98-004-3416, 98-018-3415, 98-002-4701 and 98-003-5538, respectively.

5.4 Hardness and microstructure

LENTM processed and oxidized samples were mounted in phenolic thermoset resin with the top surface exposed. This plane was grounded 1 mm exposing the core region of the cube sample. The sample surface was then mechanically polished with SiC paper of grit size 2000, and further polished with alumina-DI water suspension at 1 μ m, 0.3 μ m and 0.05 μ m particle size. Samples were then ultrasonically cleaned for 15 min in 200 proof ethanol for removal of polishing media, followed by drying in air. Microhardness measurements were performed using a Phase II Plus, Micro Vickers hardness tester (Model# 900-391, Upper Saddle River, NJ, USA), with a loading of 200 g and a dwell time of 15 s. Six indentations were in the proximity of the core. Etching was done using Kroll's Reagent (46 ml DI water, 3 ml nitric acid, 1 ml hydrofluoric acid) by submersion for 15 s under agitation. Once etched, samples were rinsed in DI water, ultrasonically cleaned in 200 proof ethanol and allowed to dry in air. Samples were then imaged using a field emission scanning electron microscope (FESEM, FEI-SIRION, Portland, OR) at an acceleration voltage of 20 kV and a working distance of 5 mm.

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Figure 1.

Mass gain curves over area with respect to oxidation time for three samples compositions. a) complete curves from 0 to 50 h, 3BN only acceptable power fit R^2 value. b) early-stage linear model fit using Equation 6 for Cp-Ti and c) steady-state power model fit using Equation 5 for Cp-Ti and 6BN.

Figure 2.
XRD spectra for LENSTM processed Cp-Ti, 3BN and 6BN compositions.

Figure 3.

Instantaneous parabolic constant (k_p) derived by use of Equation 8, with respect to time for three TGA sample compositions for 50 h.

Figure 4.

SEM micrographs of sample cube cores at a-c) 0 h, d-f) 25 h and g-i) 50 h TGA for varying BN concentration. Note: larger images follow 50 μm scale bar while insets follow 10 μm scale bar, as displayed.

Figure 5. High magnification SEM micrograph of 3BN and 6BN samples at a, b) 0 h and c, d) 50 h TGA testing showing needle-like precipitate formation and lack of plate-like TiN microstructure at 50 h. Note: all images follow 20 μm scale bar.

Figure 6.

Vickers hardness of three compositions and three time points – LENSTM processed (0 h), 25 h TGA at 1000 °C and 50 h TGA at 1000 °C (n=6).

Figure 7.
Low magnification SEM micrograph of Cp-Ti sample after isothermal TGA testing at 1000 °C, complete spallation of oxide layer is observed.

Figure 8. Elemental dot mapping of nitrogen (N) and titanium (Ti) for 25 h TGA samples, a) Cp-Ti, b) 6BN. N pixel intensity variation non-distinguishable between the two samples.

Figure 9. Ultra-high resolution through lens detector (UHR-TLD) SEM micrographs of TGA sample cube cores after 25 h testing. a) Cp-Ti, b) 3BN and c) 6BN. Note: all images follow 10 μm scale bar.

Table I.

Oxidation rates for three sample compositions at two TGA time points. Linear constants (k_l) using Equation 6, diffusion rate constants (k) using Equation 5 and index of oxidation law (n) values for the three sample compositions.

Oxidation Rate	Early-stage (10^{-2} mass%·min ⁻¹)	Long-term (10^{-2} mass%·min ⁻¹)	k_l	k	n
Cp-Ti	6.07	0.49	6.29	9.28	1.54
Cp-Ti + 3%BN	1.92	0.4	-	3.14	2.40
Cp-Ti + 6%BN	1.42	0.24	1.71	4.81	2.06