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Oxidation resistance of spark plasma sintered Ti6Al4V-TiN composites

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ABSTRACT

This work investigate the elevated temperature oxidation of Ti6Al4V and Ti6Al4V-xTiN composites using thermal gravimetric analyser (TGA) in air at 45–800 °C. Samples prepared for the study were developed by spark plasms sintering technique at a temperature of 1000 °C with a holding time of 6 min under a pressure of 50 MPa. The alloy was admixed with varying proportions of TiN varying from 5 to 15 wt% and the effect of the ceramic additions on the thermally gravimetric analyzed samples were investigated. Scanning electron microscope attached with energy dispersive spectroscopy (SEM-EDS) was used to explore the oxide layer formed on the surface of the samples. The phases present in the oxidized samples were observed by energy dispersive X-ray diffraction spectrometer (XRD). Microhardness property was studied by the means of high impact diamond Dura scan micro hardness tester. The results showed that the reinforced Ti6Al4V with TiN significantly improved the oxidation resistance, and hardness of Ti6Al4V alloy which is compactable and beneficial for aerospace application. Ti-6Al-4V alloy reinforced with 5 wt %TiN yielded better results, with improved hardness value of 881.15 HV and less weight gain which indicates high temperature oxidation resistance.

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1. Introduction

Spark plasma sintering (SPS) is a new remarkable technique for producing and consolidating a large variety of both novel and traditional materials [1,2]. This technique has emerged as one of the most important and effective technique in a generation. It allows very fast heating and cooling rates, short holding times, and the possibility to obtain fully dense samples at comparatively low sintering temperatures [2].

Titanium is the fourth most abundant and most widely used metal in structural components and aerospace industry [3–5]. The high usage of titanium and its alloys is attributed to the excellent properties they exhibit such as light weight, high strength, resistance to corrosion and hardness [6,7]. These exceptional properties of titanium and its alloys makes them the most appropriate materials for a wide range of uses. Titanium and its alloys find use in low temperature areas below 550 °C [7]. However, at elevated temperatures exceeding 600 °C, conventional titanium alloys can be ignited and burned, which limits their application for advanced aero-engines [7,8].

It is for this reason that specific properties of titanium and its alloys is improved to be competitive with high strength steel or Ni-based alloys. The addition of ceramic particulates has been researched to improve the hardness, and oxidation resistance of titanium and its alloys [9]. However, it is important and ideal that the ceramic particulates as a reinforcement be of high hardness, high rigidity, chemical stability and compatibility with the matrix at the sintering temperatures.

Many researchers investigated the morphology, mechanical and corrosion properties of Ti6Al4V alloy reinforced with various ceramic particulates [10,11]. Some of the reinforcing particulates that have been used include, SiC, TiC, TiB_2, Al_2O_3, Si_3N_4, Y_2O_3 and B_4C etc [11]. Amid these reinforcements, titanium nitride (TiN) has been recognized as a very prominent reinforcement for titanium matrix composites due to its low electrical resistivity, high melting point, chemical and metallurgical stability and exceptional mechanical properties [12].

Nandwana et al. [13], explored the formation of Equiaxed alpha and titanium nitride precipitates in spark plasma sintered TiB/Ti6Al4V composites and a highly refined and homogenous distribution of TiN precipitates was observed within the matrix which resulted in improved mechanical properties of the alloy and, Yanjun et al. [14], investigated the rapid preparation of TiC reinforced Ti6Al4V based composites by carburizing method through spark

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plasma sintering technique.

Kgoete et al. [15] investigated the influence of Si_3N_4 on Ti6Al4V via spark plasma sintering focusing on microstructure, corrosion and thermal stability. The experimental results revealed that the microstructure, corrosion resistance and thermal stability properties of the material was improved by the addition of Si_3N_4. The ceramic particulate is considered as a high corrosion resistant material which enhanced the corrosion resistance and thermal properties of the composites hence providing protection.

Vojtech et al. [7], explored the elevated temperature oxidation of titanium-silicon alloys. The alloys were exposed to temperatures in the range of 650–850 °C for up to 320 h. The oxidation kinetics as well as the composition and morphology of scales were investigated and compared with those of pure titanium. The authors obtained a course eutectoid Ti_5Si_3 particles in the TiSi8 alloy which played a key role in the oxidation process. The oxidation resistance of the alloy was improved by the addition on Si.

Mitsuo et al. [16], studied the improvement of high -temperature oxidation of titanium nitride and titanium carbide films by aluminum ion implantation. The oxidized surface of as-deposited TiN films had rutile TiO_2 above the temperature of 873 K, and those of as-deposited TiC films had anatase TiO_2 above the temperature of 873 K. The authors found that Al oxides formed on the Al implanted TiN and TiC films improved the oxidation of these films. In this work, the influence of high temperature oxidation on the mechanical, electrochemical and thermal properties of Ti6Al4V alloy and Ti6Al4V-xTiN composites fabricated through spark plasm sintering technique are investigated with the intention to explore the high temperature properties of the composites as a result of high temperature oxidation.

2. Experimental procedure

2.1. Spark plasma sintering

Titanium powder (Ti6Al4V) of (45–90 μm particle spherical, from TLS Technik GmbH) and titanium nitride powder (TiN) of (<3 μm particle size from sigma Aldrich) were blended using a tubular mixer at a speed of 49 rpm at room temperature for 4 h as per the chemistry proportions recorded in Table 1. Tubular mixing involves mixing of immensely hard particulates with very light ones, mixing of insignificant amounts of powders into larger volumes, mixing of brittle grains without disintegrating and successful blending of various particles with different diameters. The equipment works by breaking powder particles and mix them by impact and grinding. After mixing the samples were prepared for consolidation. Spark plasma sintering (SPS FCT Systeme GmbH) model was employed to consolidate Ti6Al4V and Ti6Al4V-xTiN powders respectively. ASTM B183-79 (2014), standard practice for powder formation and development. The powders were loaded in a 30 mm diameter graphite dies of 5 mm thickness [5]. The consolidation was done at a temperature of 1000 °C, heating rate of 100 °C/min, and dwelling time of 6 min at a pressure of 50Mpa under argon (Ar) atmosphere [15].

2.2. Densification studies

To investigate the effect of TiN particles on Ti6Al4V alloy, density measurements were taken using Archimedes' principle. The deionized water served as the immersion liquid for measuring the weight of the samples in water and in air. The densitometer calculated the density of the compacts automatically and the recorded densities were an average of five measurements [15].

Table 1
Starting materials.

Powder	Particle Size (μm)	Density (g/m^3)	Purity
Ti6Al4V alloy	>45	4.43	>99
Titanium Nitride	<3	5.40	>99

2.3. Oxidation studies

After densification measurements, thermal gravimetric analyser (TGA) was used for oxidation resistance studies. The samples were studied at a temperature of 45 °C to 800 °C at a heating rate of 10 °C/min in an oxygen atmosphere. The equipment has a sample pan that is supported by a precision balance with a purge gas. The sample pan inside the furnace is heated and cooled down during the experiment and the mass of the sample is monitored as a function of temperature change with time in a controlled atmosphere.

2.4. Microstructural and microhardness studies

To investigate the oxide layer formed on the surface of the Ti6Al4V and Ti6Al4V-xTiN composites scanning electron microscopy attached with energy dispersive spectroscopy (SEM-EDS) and microhardness using emco microhardness tester with a dura scan diamond indeter was employed. Indentations were made across the thermally oxidized sintered samples surface at three locations using a load of 10 g for 10sec and the average hardness was used as a final microhardness of the compacts.

3. Results and discussion

3.1. Morphological studies

Fig. 1 (a) and (b) displays the SEM morphology of thermally oxidized Ti6Al4V and Ti6Al4V-xTiN respectively from 45 to 800 °C for 95 min. The morphology of the oxide layer shows well dispersed and homogeneous crystal distribution. Kgoete et al. [15] and Guleryuz and Cimenoglu [17] illustrated that the tendency of titanium for oxygen results in the formation of a thin oxide layer that forms on the surface of a sample at room temperature. Anatase and rutile are the most common forms of TiO_2 of the oxide layer that forms [18]. Though at elevated temperatures above 400 °C, instead of a thin oxide layer a thick layer form. This thick oxide scale is not adherent but defective and brittle. Observing figure (a) the oxide layer on the surface of the sample is thick illustrating the easy wear of the oxide layer in high wear, corrosive and elevated temperature applications.

Figure (b) shows the morphology of Ti6Al4V-xTiN composites. A thin adherent layer can be observed on the sample. This is attributed to the TiN addition which serves a barrier for oxygen diffusion on the surface of the sample. A material that is said to be resistant to oxidation is the one which creates a relatively thin and mechanically stable oxide layer that can bring extraordinary protection against corrosion and elevated temperature wear [15,17]. Observing figure (b) the thin oxide layer illustrates the improved elevated temperature properties of the alloy which indicates that addition of ceramic does improve the oxidation resistance of Ti6Al4V alloy. The apparent thin oxide scale formed on the surface of the composites consists of $Ti0_2$, Al_20_3, $V0_2$ and NO as shown in Fig. 5. These observed oxides are the reason for the achieved high oxidation resistance.

Fig. 2 shows the weight change of the composites because of oxidation between 45 and 800 °C. The onset temperature of Ti6Al4V is about 650 °C where there is a rapid drop in mass which indicates elevated temperature instability and the starting

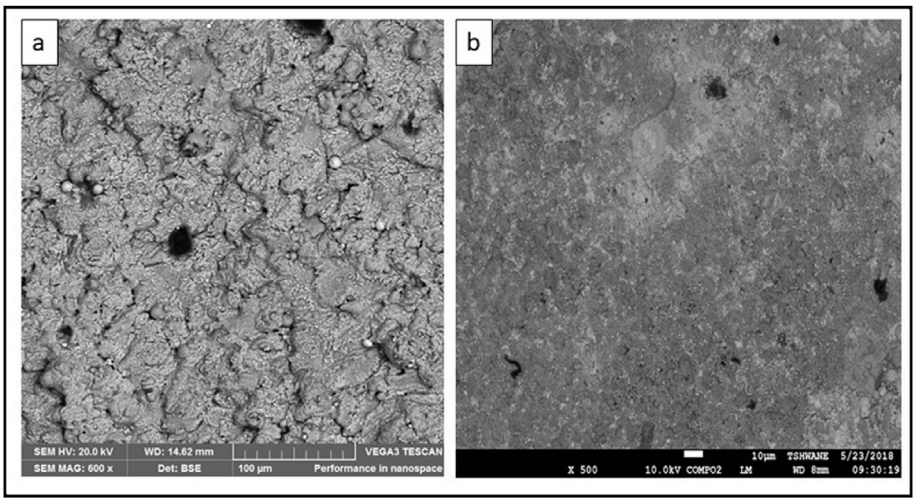

Fig. 1. SEM images of a) Ti6Al4V and b) Ti6Al4V-xTiN.

temperatures of the oxidized Ti6Al4V-xTiN is about 700 °C and the graphs shows a parabolic form which denotes the development of a protective oxide thin scale which has been mentioned to be the reason for the improved elevated temperature oxidation resistance. It can be observed that reinforced Ti6Al4V with xTiN exhibit the lowest material loss as compared to the unreinforced Ti6Al4V alloy.

The oxidation behavior of Ti6Al4V-xTiN alloys was considered using thermal gravimetric analysis (TGA). Fig. 3 displays the result of the TGA experiment after Ti6Al4V and Ti6Al4V-xTiN alloys were heated from 45 to 800 °C at a heating rate of 10 °C/min in oxygen. The compacts were oxidized and the weight gain was related with the unreinforced compacts. All the compacts revealed parabolic increases in mass through oxidation process. Observing the graphs, it can be observed that the weight gain of the Ti6Al4V-xTiN were significantly less than the unreinforced alloy which indicates that the addition of TiN restricts the oxidation rate of the alloy, resulting in high oxidation protection ability [19]. The increasing addition of TiN decreased the weight gain of the developed compacts.

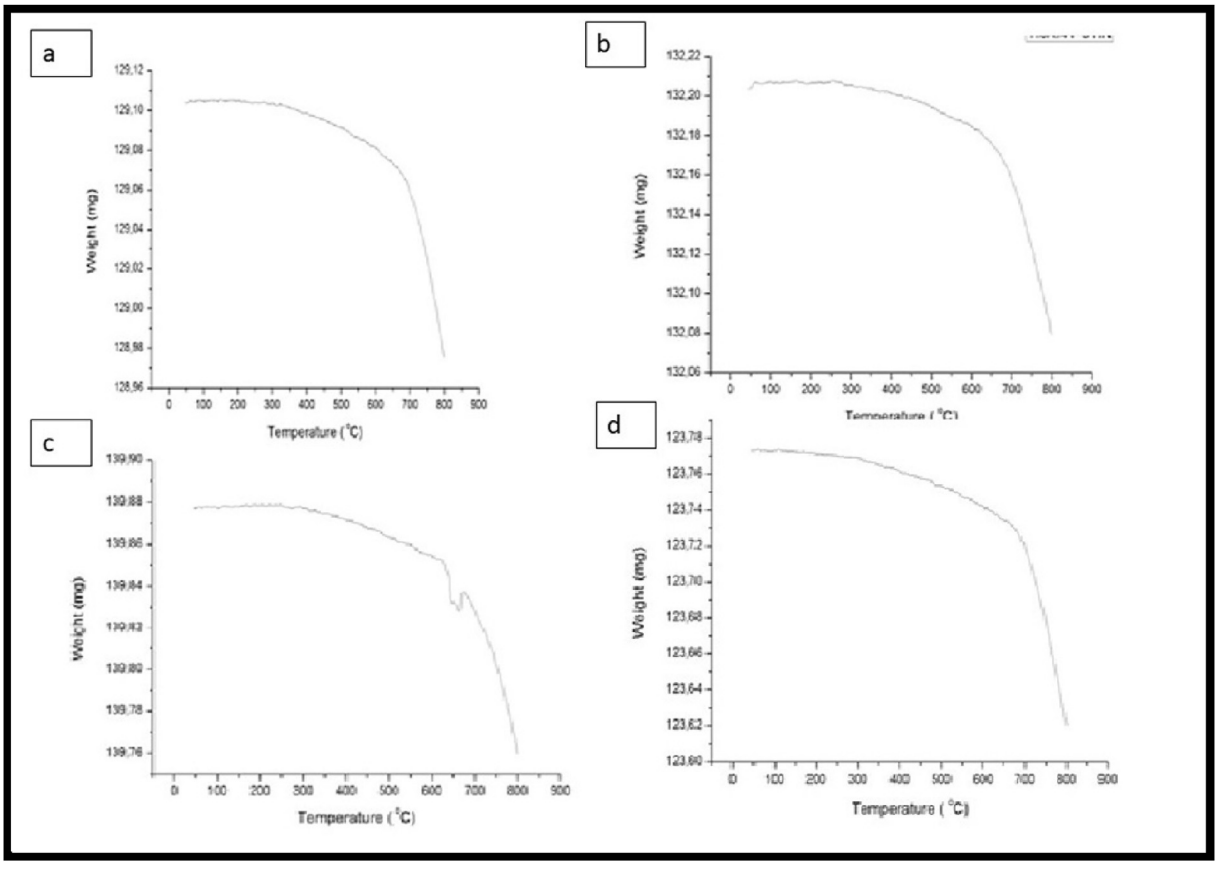

Fig. 2. Thermal oxidation graphs of a) Ti6Al4V, b) Ti6Al4V-5TiN, c) Ti6Al4V-10TiN and d) Ti6Al4V-15TiN.

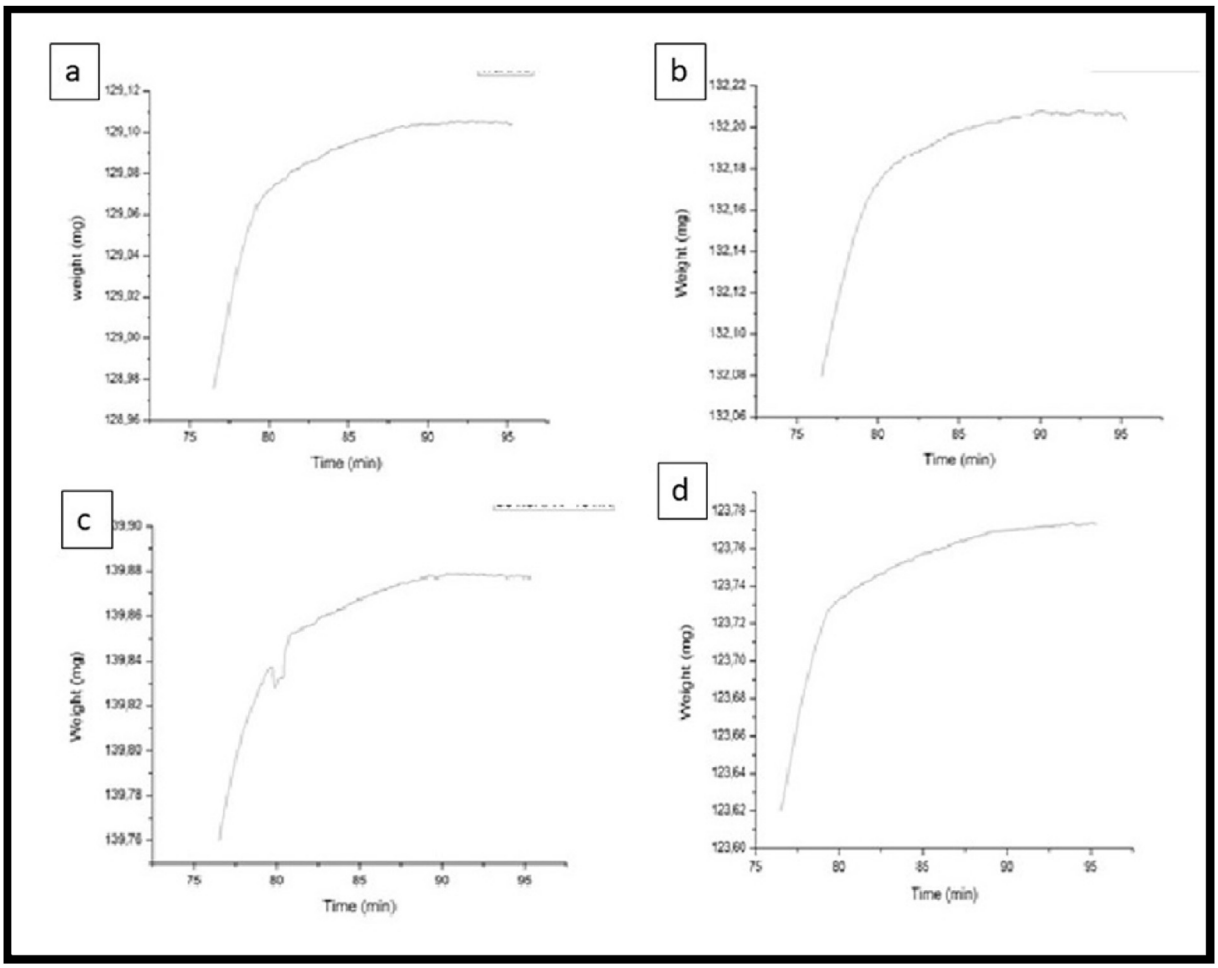

Fig. 3. Shows the variation of weight gain against time for a) Ti6Al4V, b) Ti6Al4V-5TiN, c) Ti6Al4V-10TiN and d) Ti6Al4V-15TiN.

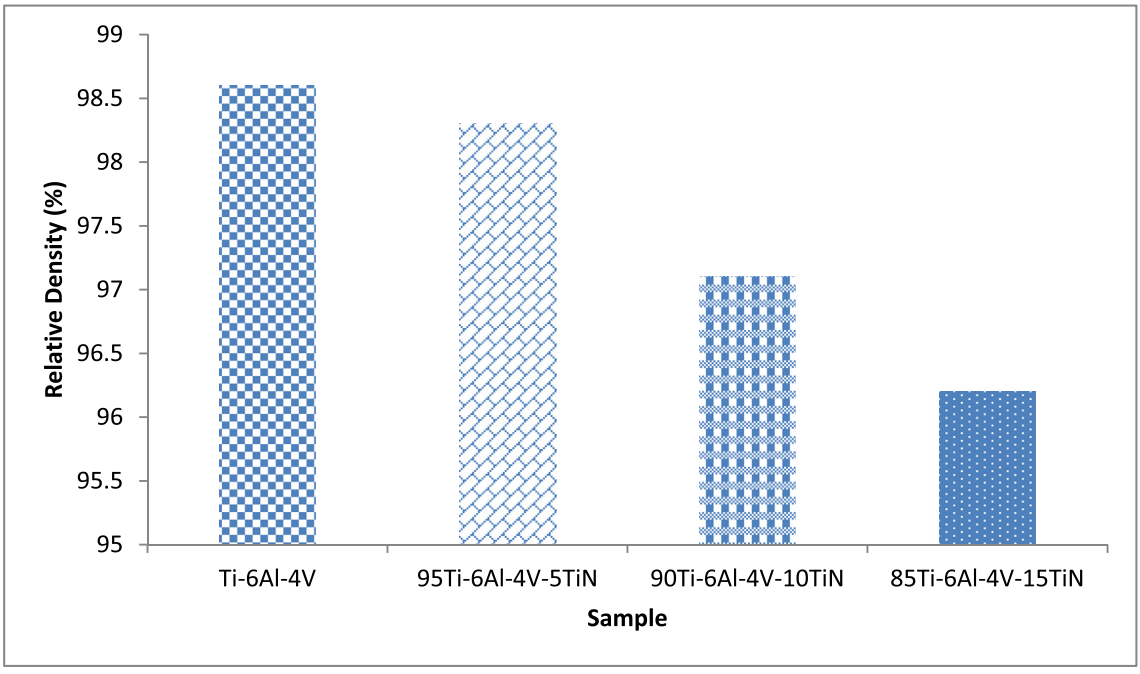

Fig. 4. Relative densities of the sintered compacts of Ti-6Al-4V and developed Ti-6Al-4V-TiN.

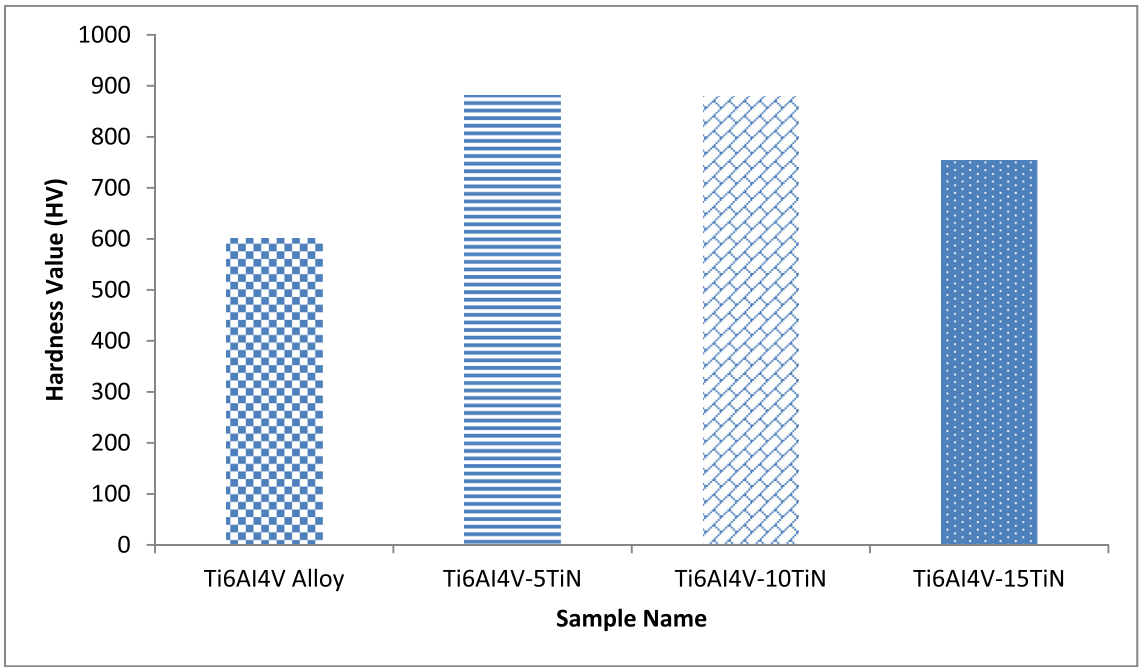

Fig. 5. Hardness properties of Ti6Al4V and Ti6Al4V-xTiN sintered composites.

3.2. Densification and microhardness properties

Subsequent to spark plasma sintering, density measurements were taken, and the relative densities of the composites can be observed in Fig. 4. The density of the compacts decreased with TiN addition. This may be due to the nature of TiN since well Falodun et al. [20] also obtained a decrease in relative density with increasing nano-sized TiN particulates in the matrix. The achieved decrease in relative density does not spontaneously results in poor mechanical, corrosion and oxidation resistance of the developed composites.

Fig. 5 displays the influence of varying TiN ceramic additions on the hardness characteristics of the thermally oxidized Ti6Al4V and Ti6Al4V-xTiN composites. Observing Fig. 5, microhardness of the oxide layer of Ti6Al4V is 601.49HV and the average microhardness for Ti6Al4V-xTiN is 879.96 HV. The obtained microhardness value is 278.47 HV more as compared to the Ti6Al4V alloy. This may be due to the hard-adherent oxide layer formed on the surface of the specimen. The improved hardness value is responsible for the improved elevated temperature properties of the alloy.

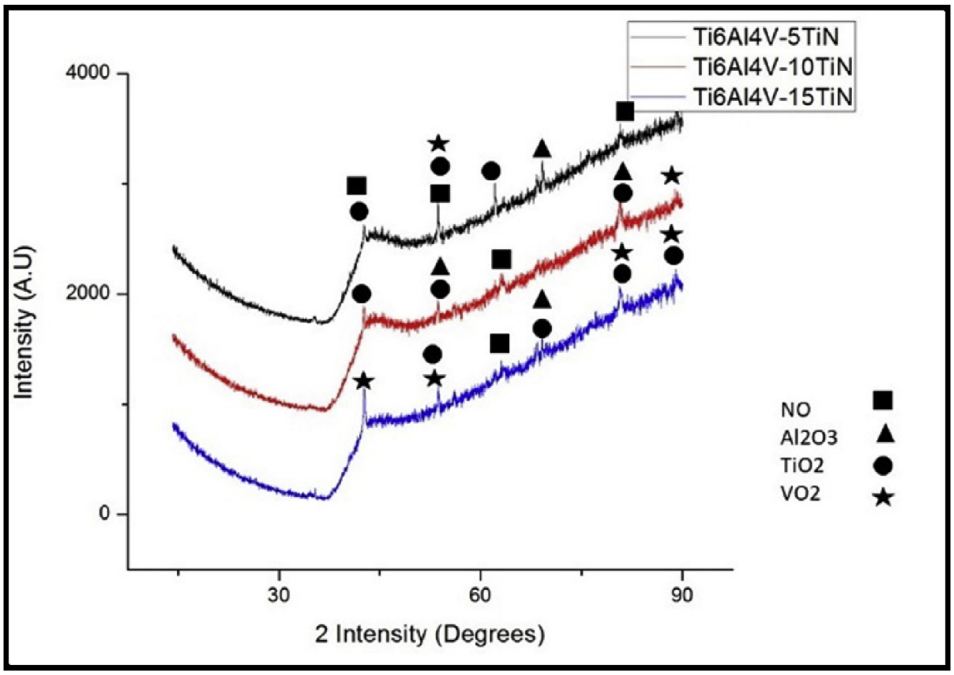

Fig. 6. XRD patterns of Ti6Al4V-xTiN sintered composites.

3.3. Phase formation

Fig. 6 illustrates the XRD patterns of the thermally oxidized Ti6Al4V-xTiN composites. It can be seen that all the Ti6Al4V-xTiN alloys exhibit the peaks of TiO_2, V_2O_3, Al_2O_3 and NO. The phases present are attributed to the reaction of the elements with oxygen at elevated temperatures. The formation of these phases is beneficial to the improved high temperature oxidation of the composites.

4. Conclusion

In this research, three Ti6Al4V alloy, namely Ti6Al4V-5wt%TiN, Ti6Al4V-10 wt%TiN and Ti6Al4V-15 wt%TiN have been designed and developed through spark plasma sintering technique. The composites undergone thermal gravimetric analysis and after the analysis, the microstructure, mechanical properties, and phase evaluation of the alloys have been relatively investigated. The core conclusions are as follows:

1. The Ti6Al4V alloy reinforced with TiN was thermally oxidized at 45–800 °C to produce hard adherent surface layers.
2. The addition on TiN resulted in the formation on a thin adherent layer resulting in improved high temperature properties of the alloy.
3. After thermal oxidation a significant increase in surface hardness (601.49HV to 838.24 HV) was achieved due to formation of a hard adherent oxide layer and an oxygen diffusion zone beneath it.
4. Oxidation treatment of Ti6Al4V-xTiN greatly improves the mechanical and thermal properties of the alloy at 800 °C.

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