Influence of sintering temperature on densification, microstructure and mechanical properties of Ti-6Ni alloy developed via spark plasma sintering

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Abstract. Titanium is used extensively in various engineering applications as a result of its unique physical, chemical and mechanical properties. However, the difficulty encountered in fabricating a fully densified titanium sample informed the introduction of alloying elements into the matrix in order to form a liquid phase and enhance sinterability. This work explored the influence of sintering temperature on the densification, microstructure and mechanical properties of Ti-6Ni alloy developed via spark plasma sintering at varying temperature from 850 °C to 1200 °C in a vacuum, under isothermal holding time, heating rate and applied pressure of 10 min, 100 °C/min and 50 MPa respectively. Characterization of the mixed powder and bulk sintered sample were carried out with the aid of scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscope (EDS) and X-ray diffraction (XRD). Relative density and hardness of the samples were determined following the Archimedes and Vickers method respectively. The SEM results indicated the presence of multiple phases in the microstructure of the sintered samples. These phases were confirmed by the EDS and XRD analysis results, as the intermetallics of Ti-Ni. Densifications above 98%, was achieved and the hardness values were found to vary with the densification of the sintered alloy, across the investigated sintering temperatures.

1. Introduction

Development of new materials that are capable of withstanding the challenges of high temperature applications has been a major challenge to researchers in different fields. However, modification of the properties of the existing materials with known history, has received the attention of researchers as this saves cost, time and accurate prediction of their performance in service can be made. Titanium occupies an important position among the committee of metals capable of performing excellently in high temperature applications [1]. Titanium and its alloys have progressively gaining the attention of the researchers as a result of their attractive intrinsic properties which made them one of the sought after candidate materials in aerospace, automobile, marine, biomedical, chemical and industrial applications, requiring high strength-to-weight ratio, excellent corrosion resistance, biocompatibility and high operating temperature. Despite these attractive properties, further utilization of this material is being threatened by the high cost of its extraction and manufacturing of the final product [2, 3].
the high level of attraction between titanium and oxygen results in oxide formation on the surface of the pure titanium powder. Consequently, this reduces the chemical reactivity of the surface and creates difficulty for densification during the sintering of titanium [4, 5]. Improvement in the sinterability of pure titanium powder can be achieved through the addition of elements that have the capacity to ease diffusion and improve sinterability through the formation of the liquid phase [6]. The use of powder metallurgy methods such as the spark plasma sintering (SPS) technology [7] which combine joule heating and spark discharge generated between powders due to the applied current, pressure and pulse voltage, to rid the surface of the powders of oxide films and enhance self-diffusion of titanium around the neck area and subsequent growth of this region [8].

It has been confirmed that the addition of a small quantity of nickel to titanium improves the ability of titanium to diffuse and enhances densification [9-11]. Nickel achieves this through reduction of the activation energy needed for self-diffusion of titanium which then leads to enhanced densification [12]. Also, during the spark plasma sintering process, diffusion phenomena increase and transfer of materials take place as a result of the plasma developed between the powders particles. This results in the removal of the oxide impurities from the surface of the materials. Furthermore, the joule heating effect and pressure-assisted plastic deformation of the powders enhanced sinterability and densification [7, 13, 14].

Previously, studies were conducted on dilatometric sintering of titanium with small additions of nickel [12, 15]. The results of these works showed that highest densification was achieved at a temperature just below the solidus line while swelling was observed in samples sintered at temperatures above the solidus line. To this end, this work studied the influence of spark plasma sintering temperature, on the densification behaviour, microstructure and how this affects the mechanical property of Ti-6Ni alloy.

2. Experimental Procedure

2.1. Powder preparation and characterization

Commercially sourced CP-Ti Grade1 (TLS Technik GmbH & Co, Germany) and Ni (FlomasterTM metal powder, F.J. Brodmann & Co., ltd., USA) powders of particles size < 25 μm and 0.5-0.3 μm respectively were utilized for this research. Ni and Ti powders were weighed based on the different wt% (Ti-6Ni). The weighed powders were discharged into a 250 ml container, filled up to 20% level and arranged axially into a TF2, Turbular shaker mixer. The powder mixture was blended under a rotational and translational speed of 101 rpm for 8 h.

2.2. Powder consolidation

The admixed powders were weighed and emptied into a non-conducting, graphite die, with an outer diameter of 50 mm and an inner diameter of 30 mm respectively. The graphite die was lined with graphite foil to minimize the heat loss due to radiation and prevent difficulty in removing the samples after sintering. The prepared samples were sintered using spark plasma sintering system HHPD-25, FCT Systeme GmbH, Germany under different sintering temperatures of 850, 1100 and 1200 °C. The applied pressure, isothermal holding time and heating rate were kept at 50 MPa, 10 min and 100 °C/min respectively. The schematic features of the spark plasma sintering equipment are shown in Figure 1.

The temperature was measured with the aid of an external pyrometer with sensitivity at 250 °C, located at a distance of about 3 mm above the sample. At the expiration of the holding time, the samples were allowed to cool down to the ambient temperature in the furnace. Subsequently, the sintered samples were sandblasted to remove the graphite foil layer and the density of the sintered samples was measured by using the Archimedes technique. The relative density, \( R_p \) was obtained using equation 1.

\[
R_p = 100\left(\frac{\rho_{exp}}{\rho_{th}}\right)
\]  

where, \( \rho_{exp} \) and \( \rho_{th} \) are the experimental and theoretical density respectively.
2.3. Microstructural and phase analysis

Samples for metallographic analysis were sectioned, ground with silicon carbide paper from 320 up to 2400 grit size. Polishing was conducted with diamond pastes of particle sizes 9, 6, 3 and 1 μm. The prepared samples were subsequently etched using Kroll reagent (3% HF, 5% HNO3 and 92% H2O) for 20 s and analyzed by using field electron scanning electron microscope (JOEL JSM-7600F) in conjunction with an energy-dispersive X-ray spectroscope (EDS) detector. Phase Identification was carried out with the aid of PW1710 Philips, X-ray diffractometer, utilizing Cu Kα radiation operated at 40 kV and 40 mA with 2θ ranges from 5 to 90 and a step size of 0.01. The obtained diffraction patterns were compared with the database of the equipment, using X’Pert High Score Plus software.

2.4. Hardness measurement

The Vickers hardness (HV) of the sintered samples was determined under ambient temperature using Future-tech microhardness tester. The test load and dwell time were maintained at 1000 gf and 15 s respectively. The reported microhardness value was obtained as an arithmetic mean of ten consecutive measurements for an individual sample.

3. Results and Discussion

3.1. Microstructure and phase analysis

SEM micrograph of the turbula-mixed powders of elemental titanium and nickel are shown in Figure 2(a). The admixed Ti-6Ni powder consists of regular, spherical and non-porous Ti powders which suggest that the powder was formed by gas atomization while the Ni powders appeared as an agglomeration of small, non-porous particles which may be attributed to water atomization production route. The microstructures of the sintered Ti-6Ni samples sintered at 850, 1100 and 1200 °C are shown in Figure 2b-d respectively. The formation of the lamella and acicular-like structures were observed in the micrographs of the sintered alloys at low and high temperatures respectively. These structures consist of alternating arrangements of dark α-Ti phase and Ti-Ni rich whitish phase, as shown in Figure 2(e) and (f). The intermetallics were formed due to the interactions between nickel and titanium over the sintering temperatures under consideration. Nickel reacts with titanium at temperatures above the transus temperature due to its solubility in β-Ti to form a solid solution of Ti-Ni. However, its limited solubility in α-Ti resulted in the formation of intermetallics on cooling down to the room temperature [12] as observed in XRD patterns presented in Figure 3.

Lamella arrangements of white patches and bright spots within a dark matrix of α-Ti were observed in sample sintered at 850 °C (Figure 2b), this can be ascribed to the interaction between titanium and nickel at low operating temperature, as diffusion also depends on the temperature of the system. Fine and neatly arranged acicular-like structures and bright spots were also observed in Figure 2c as the operating temperature increased to 1100 °C. This can be attributed to the enhanced diffusion of nickel which provided enabling system for self-diffusion of Ti for Ti-Ti interactions and formation of liquid phase.
which lowers the energy required for the reaction between Ti and Ni to occur. Hence, the improved nucleation and growth of the acicular-like structure, as shown in Figure 2c. Sample sintered at 1200 °C, shows no noticeable bright spots but distorted acicular-like structure (Figure 2d) was observed. The distorted structure can be traced to the loss of Ti-Ni rich liquid phase [10] which solidified on the graphite punch during sintering, thereby depriving the system the much needed Ti-Ni rich liquid required for the growth of the intermetallic phase(s) within the matrix. The loss of the Ti-Ni rich liquid can be attributed to the composition of the sintered alloy and temperature of the operation. The 6 wt% Ni and the operating sintering temperature of 1200 °C correspond to the boundary between the β single-phase field and the dual-phase field of β+L (solidus line) on the Ti-Ni binary phase diagram. At this location, there is a high possibility of formation of the liquid phase and its subsequent expansion [15] resulted in the observed solidification of the sipped out liquid, on the body of the graphite punch.

![Figure 2. SEM Micrographs showing (a) backscattered image of the Ti-6Ni Turbula mixed powder (b) secondary electron image of Ti-6Ni sintered at 850 °C (c) secondary electron image of Ti-6Ni sintered at 1100 °C (d) secondary electron image of Ti-6Ni sintered at 1200 °C (e) EDS of whitish part of the acicular-like structure (f) EDS of darkish part of the acicular-like structure.](image)

Identification of phases formed as a result of the reactions during sintering was conducted using X-ray diffraction analysis. The diffraction patterns obtained from analysed Ti-6Ni sintered alloys at different sintering temperature are shown in Figure 3. The patterns show a consistent existence of hcp, α-Ti (dark), TiNi$_2$ (bright) and fcc, Ti$_2$Ni (whitish) phases within the matrix. The Ti$_2$Ni and TiNi$_2$ intermetallic phases were formed in the Ti-Ni rich regions as shown in Figure 2(e) and (f) through the diffusion of nickel into the crystalline structure of titanium. The ability of Ni to lower the activation energy of Ti, allows the reaction between Ti and Ni to take place below the eutectoid temperature of 862 °C. Hence, the formation of the solid solution of Ni in β-Ti which upon cooling to ambient temperature forms Ti$_2$Ni and TiNi$_2$ intermetallics due to the limited solubility of Ni in α-Ti. The phase constitutions of the investigated alloys at different sintering temperature as revealed in Figure 3 are shown in Table 1.
Table 1. Effects of sintering temperature on the phase constitution of the investigated alloys

| Sample designation | Sintering temperature (°C) | α-Ti phase content, vol. % | TiNi phase content, vol. % | TiNi₂ phase content, vol. % |
|--------------------|-----------------------------|---------------------------|--------------------------|---------------------|
| Ti-6Ni             | 850                         | 58                        | 10                       | 32                  |
|                    | 1100                        | 50                        | 9                        | 41                  |
|                    | 1200                        | 82                        | 18                       | -                   |

Figure 3. Diffraction patterns of the sintered Ti-6Ni samples under different sintering temperatures.

3.2. Relative density and microhardness

Table 2 shows the summary of the properties of the sintered Ti-6Ni over the investigated sintering temperatures. It can be observed that the sintered samples displayed high level of densification whereas their microhardness values differ. A relative density of 99.79% with microhardness value of 294±3.43 HV was observed in samples sintered at 850 °C. These values increased to 99.87% and 299±5.10 HV for sample sintered at 1100 °C. However, a decline in the relative density (98.6%) and microhardness value (247±12.35 HV) was observed in sample sintered at 1200 °C. The observed trend can be attributed to the influence of nickel addition in aiding self-diffusion of titanium and the formation of hard and brittle Ti₃Ni [9] and TiNi₂ intermetallics during the sintering of Ti-6Ni alloys. According to Riva et al. [17], the occurrence of the non-stoichiometric, metastable phases within the matrix of an alloy can be attributed to the rapid cooling of the alloys from the elevated sintering temperatures. The presence of these metastable phases in association with the stable phases of Ti-Ni was confirmed in the work of Fuji and Yamamoto [18], Sadmezhaad and Selahi [19] and Rominiyi et al. [16].

Table 2. Summary of the investigated alloys properties.

| Samples designation | Sintering temperature (°C) | Theoretical density, ρₜ (g/cm³) | Experimental density, ρₑ (g/cm³) | Relative density (%) | Microhardness (HV) |
|---------------------|---------------------------|---------------------------------|---------------------------------|---------------------|-------------------|
| Ti-6Ni              | 850                       | 4.648                           | 4.638                           | 99.79±0.29          | 294±3.43          |
| Ti-6Ni              | 1100                      | 4.648                           | 4.642                           | 99.87±0.21          | 299±5.10          |
| Ti-6Ni              | 1200                      | 4.648                           | 4.582                           | 98.58±1.42          | 247±12.35         |
The existence of TiNi$_2$ (hcp) and Ti$_2$Ni (fcc) intermetallic phases within the matrix of the sintered alloys resulted in structure mismatch, distortion and development of lattice strain in the material. The volume of these intermetallics is observed to increase with increasing sintering temperature (Table 1). Consequently, this increased the resistance to the dislocation movement during indentation and this was responsible for the increase in hardness observed in the sintered alloy at 1100 °C when compared with the hardness of sample sintered at 850 °C. However, sample sintered at 1200 °C was expected to possess the highest microhardness value but the loss of Ti-Ni rich liquid, deprived the matrix the needed volume of intermetallics (Table 1 and Figure 3) within the matrix. This resulted in less distortion within the matrix (Figure 2d) and few obstructions are provided in the path of dislocation during indentation. Hence, the lowest microhardness value observed in the sample sintered at 1200 °C.

4. Conclusion
This work investigated the Influence of sintering temperature on densification, microstructure and mechanical properties of Ti-6Ni alloy using spark plasma sintering technique. Based on the extent of work done in this research, it was concluded that increasing the spark plasma sintering temperature from 850 °C to 1100 °C at constant pressure, heating rate and dwelling time of 50 MPa, 100 °C and 10 min respectively improved the microstructure, enhance densification and increase the microhardness value while further increase in temperature up to 1200 °C yielded deteriorated microstructure, decline in densification and the microhardness value of the spark plasma sintered Ti-6Ni alloy. However, it is speculated that lowering the pressure at the same temperature of 1200 °C can prevent loss of the Ti-Ni rich liquid phase during spark plasma sintering thereby achieving higher densification and hardness than what was obtained in the case of sample sintered at 50 MPa and 1200 °C in this work.

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