Fabrication and characterization of titanium-nickel-zirconia matrix composites prepared by spark plasma sintering

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Abstract

Ti–Ni–ZrO_2 composites were prepared by spark plasma sintering (SPS). The effect of ZrO_2 content on the densification, microstructure and microhardness properties of the composites were investigated. Samples were characterized by SEM, EDS and XRD analyses. Noticeably, SPS process under the sintering conditions was achieved at a sintering temperature of 950 ºC, for 10 min holding time, at 100 °C/min of heating rate and at an applied pressure of 50 MPa. This resulted in maximum densification of the powder compact and the formation of a distinguishable spherical globules rich in Ni surrounding the retained Ti. Gradient composition distribution of ZrO_2 at the grain boundaries resulted into pinning effect of the grain growth. As the ZrO_2 content increased from 5 to 10 vol.%, it was accompanied by a significant increase in hardness values of the sintered composites from 480 to 713 HV.

Keywords: Spark plasma sintering; Zirconia; Titanium; Composites; Pinning effect

1. Introduction

For many years, the development of new materials (alloys or composites) has been the driving force for technological advancement. From heavy to light industries, the need for new materials is growing especially light metals such as aluminium, magnesium and

titanium. In recent times, there has been an increase in the number of conferences/symposia focusing solely on light metals and light metals technology. This could be as a result of the critical technological challenges encountered on such materials, due to engineering components/parts being exposed to extremely harsh environmental conditions [1]. Titanium, as a light metal finds applications in mechanical, aerospace and biomedical industries owing to its high strength to weight ratio, good resistance to corrosion, biocompatibility and osseointegration properties [2, 3].

Powder metallurgy (P/M) technique which involves sintering has been used to produce new titanium alloys/composites because of the low cost, near net-shape fabrication, increase in material yield and variation of composition [4]. Some novel sintering techniques such as hot pressing (HP) [5], hot isostatic pressing (HIP) [2, 6], microwave sintering [4, 7] and spark plasma sintering (SPS) [8], have been reported for fabrication of engineering materials [9]. SPS has become a special technique for the consolidation of a different materials towards engineering advancement beacuase it offers several advantages over other conventional sintering techniques such as fast heating rates, lower sintering temperatures, short sintering time, higher sintered densities, minimal material loss during sintering and limited grain growth.

Although the SPS technique has been established to be effective for the development of different engineering materials, there is still limited scientific knowledge on the consolidation of Ti alloys reinforced with nickel and zirconia. Therefore, it becomes very necessary that more attention be paid to the study of titanium-nickel-zirconia composites developed through spark plasma. The possibility of reinforcement in metal matrix composites can change the properties of the composites so that their applications can be

broadened [4]. The relationship between the sintering temperature, densification rate and microstructure of the SPS sintered Ti composites have been investigated.

2. Materials and Methods

Commercially available cp-Ti powder (99% purity, APS 88 µm), Ni powder (99% purity, APS 88 µm) and ZrO_2 powder (99% purity, APS 44 µm) supplied by Alfa Aesar were used in this study. Fig. 1 shows the SEM morphology of the starting powders. The cp-Ti and Ni powders are spherical and non-porous [10] with very few satellites suggesting that the powders were produced through gas atomisation [11, 12] while ZrO_2 particles are round with hollow doughnut-like morphology and with many satellites. Ti, Ni and ZrO_2 powders were weighed and mixed according to the different volume ratios i.e. Ti–45Ni–5ZrO_2 and Ti–40Ni–10ZrO_2 as listed in Table 1. The weighed powders were placed in a 250 ml cylindrical plastic vessel with a powder fill level of 50 %, loaded axially, positioned in a Turbula shaker mixer and subjected to translational and rotational motions for 8 h at a speed of 49 rpm. The mixing was carried out in a dry environment. The ad-mixed powders were sintered in a vacuum environment using the SPS process (HHPD 5 manufactured by FCT Germany). The sintering parameters are presented in Table 1.

The density of the sintered samples was measured based on Archimedes' principle. Phase identification was performed using the PW1710 Philips X-ray diffractometer with Cu Kα radiation at 40 kV and 40 mA to identify the constituent phases. Diffractograms were collected over a range of 2θ between 10 and 90°, with a step size of 0.02. A search-match routine was performed using X'Pert High Score Plus software for phase identification.

Samples for metallographic examinations were sectioned using a Buehler™ Isomet 4000 linear precision saw with a diamond blade, mechanically ground with silicon carbide paper

from 220 down to 1200 grade, polished from 9 to 1 μm diamond finish, cleaned with distilled water and acetone and dried in air.

Microstructures of the powders and sintered samples were carried out in a field emission scanning electron microscopy (JEOL FE-SEM JSM-7600F) equipped with energy-dispersive X-ray spectroscope for compositional analysis. Microhardness test (Vickers) was carried out using a Future-Tech FM 700 Microhardness tester at an indent load of 100 gf ($HV_{0.1}$) and a dwelling time of 10 s. Ten indentations were taken at intervals and the average value recorded.

3. Results and discussion

Fig. 2 shows the relative densities of cp-Ti and Ti–Ni–ZrO_2 composites sintered between 850-950 °C at sintering pressure of 50 MPa. Sintered relative density of cp-Ti without Ni and ZrO_2 addition reaches 98.48% densification at a temperature of 850 °C, which is in agreement with Balaji and Kumaran [13]. On one hand, it was observed that there was a significant decrease in the relative density of Ti–45Ni–5ZrO_2 (850 °C) to 84.99% due to the presence of pores (see Fig. 3b). It must be noted that sintering titanium with addition of Ni and ZrO_2 at low temperature could result in high porosity and thus result in low sintered density. On the other hand, it was noticed that the sintered relative densities increased with an increment in sintering temperature from 850 to 950 °C (for both 5 and 10 vol.% ZrO_2). This can be attributed to the rearrangement and increasing contact points between particles which were intensified with the increasing temperature. The sintered relative density of the composites as presented in Table 1 increseases with increasing ZrO_2 content and temperature from 84.99% (Ti–45Ni–5ZrO_2(850 ºC)) to 100% (Ti–40Ni–10ZrO_2(900 ºC)). In otherwords, the addition of more ZrO_2 content could promote full densification achieved at 900 ºC [14]. Furthermore, the sintering densification process progresses at an even lower temperature range and addition of more ZrO_2 makes more significant effect. Generally, as

expected the density of the sintered compacts increased with increasing sintering temperature.

Fig. 3 shows the SEM micrographs of the cp-Ti and Ti–wNi–xZrO_2 (w = 40 and 45 vol.%; x= 5 and 10 vol.%) composites at different sintering temperature. Fig. 3(a) represents a typical SEM image of the as-sintered cp-Ti consisting of round pores and mostly α-phase. From Fig. 3(b)-(g), there is a clear indication in formation of in-situ reinforcements in the cp-Ti matrix during sintering. These formations are promoted by the presence of Ni and its high affinity with Ti, thus forming TiNi and Ni-rich spherical globules dispersed and well distributed in the Ti matrix. The white spot present in Fig. 3(b) are aggregated particles of undiffused ZrO_2.

The presence of pores around Ni-islands (spherical globules) as shown in Fig. 4(a) indicate poor sinterability of the composite at sintering temperature of 850 ºC. In other words, high content of Ni at low sintering temperature could influence the full densification of Ti. This could be responsible for the decrease in sintered relative density (84.99%) observed in Fig. 2. As sintering temperature was increased from 850 ºC to 950 ºC, and Ni content decreased from 45 vol.% to 40 vol.%, a non-porous microstructure was formed. This clearly shows that by increasing temperature, densification is promoted, also, by decreasing Ni content, the sintered relative density could increase. It is evident (in Fig. 2), that Ti–40Ni–10ZrO_2 composite sintered at 850 ºC recorded a relative density of 97% when compared with Ti–45Ni–5ZrO_2, at the same sintering temperature gave a density of 84.99%. The presence of ZrO_2 along the grain boundary as shown in Fig. 4(b) has demonstrated its binding effect.

Fig. 4(b) shows the SEM image alongside the EDS pattern with elements present in the phases. The results of the EDS analysis reveal that the light (region 1; spherical globules), grey (region 2; around the globules) and dark (region 3) phases are rich in Ni, Ti–Ni and Ti

respectively with ZrO_2 particles present at the grain boundaries which could hinder grain boundary movement as a result of pinning effect exerted by the ZrO_2 particles [14].

From Fig. 4(c), SEM investigation of neck growth showed the presence of small dispersoids comprising mostly ZrO_2 which could significantly influence sintering mechanism and grain growth during sintering. German [15] stated that small dispersoids with a close spacing are very effective in slowing grain growth as well as sintering. Also, dispersoids could provide a pinning effect on the grain boundary and cause the boundary to curve since typically the dispersoid is slow moving compared to the boundary. If the dispersoid is pulled by the boundary, then coarsening of the dispersoid occurs during sintering [16].

The X-ray diffraction spectra as a function of w/x for the Ti–wNi–xZrO_2 (w = 40 and 45; x= 5 and 10 vol.%) sintered compacts are presented in Fig. 5 and compared with the XRD spectra of commercially pure Ti (cp-Ti). The patterns of cp-Ti corresponds to hexagonal close-packed (hcp) α-Ti type structure which were generally detected without the presence of TiO_2 which indicate a complete inert environment during sintering. This result was consistent with refs [17, 18]. Diffraction peak for α-Ti (102) at a peak position 2θ=52.684º gradually becomes narrower and forms a peak overlap at 2θ=51.818º. At sintering temperature of 950 ºC/Ti–40Ni–10ZrO_2, the overlap peak disappears. This phenomenum was observed at α-Ti (100) located at 2θ=35.015º where the peak is significantly overlapping and eventually disappeared from the patterns. This could be due to microstructure inhomogeneity promoted by the presence of Ni and ZrO_2 in the matrix of cp-Ti. For all the sintered compacts, there is a minor shift in peak positions from the exact 2θ position when sintering temperature increased from 850 to 950 ºC. This may possibly be due to high micro-strain in the sintered compacts caused by the rapid heating (sintering rate of 100 ºC/min) and fast cooling during spark plasma sintering process.

Secondary phase such as Ti–Ni was detected in the patterns as a result of fast diffusion of Ni in Ti which is about two orders of magnitude [19, 20], although Ni is a preferred alloying element to cp-Ti and Ti alloys for solid state sintering [20]. Peaks of ZrO_2 were also detected as major phases in the sintered compacts suggesting that ZrO_2 is stable and unreactive [1].

The variation of microhardness measured on the polished sections of SPS-processed cp-Ti without and with addition of Ni/ZrO_2 at varying sintering temperature is shown in Fig. 6. The microhardness values of sintered composite treated at low sintering temperature of 850 ºC with 5 vol.% ZrO_2 addition was relatively the lowest compared to compacts prepared at higher sintering temperature and more ZrO_2 content. The low microhardness value could be as a result of the fact that the sintered relative density of the sample was reduced to 84.99%. Generally, the corresponding microhardness values at 5 vol.% ZrO_2 addition were considerably lower than those obtained at 10 vol.% ZrO_2. Nevertheless, the SPS-processed Ti–Ni–ZrO_2 compacts, for all the given sintering temperatures (850–950 ºC) showed superior hardness property compared to SPS-processed cp-Ti with a microhardness value of 480 HV. As it can be seen, microhardness increased from sintering temperature of 850 to 950 ºC irrespective of the Ni/ZrO_2 contents in the compacts. This enhancement of hardness could be attributed to the improvement of densification, presence of Ti–Ni and ZrO_2 phases in the cp-Ti matrix and grain refinement [10].

4. Conclusions

Ti-based (Ti–Ni–ZrO_2) composites could be fully consolidated by spark plasma sintering at a heating rate of 100 ºC/min, at 950 ºC under a pressure of 50 MPa, although the sintered relative density decreases with the addition of 45vol.%Ni–5vol.%ZrO_2,. XRD analysis and EDS confirmed the formation of in-situ reinforced Ni, TiNi and ZrO_2 phases during spark plasma

sintering.Varying ZrO_2 content can significantly influence the microstructure and microhardness values of the composites by providing pinning effect in forms of dispersoids within the neck region, slowing down grain growth and grain boundary movement. An excellent microstructure without pores and cracks was obtained with uniform distribution of Ni-rich spherical globules. Vickers hardness increases as ZrO_2 content increased from 5 to 10 vol.%.

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Table Caption

Table 1 The sample designation, sintering parameters and sintered relative density.

Figure Caption

Fig. 1. SEM morphology of the as-received powders (a) cp-Ti (b) Ni and (c) ZrO_2(8YSZ).

Fig. 2. Variation in the sintered relative density of the cp-Ti and Ti-Ni-ZrO_2 samples.

Fig. 3. Scanning electron micrographs of (a) cp-Ti, (b,c,d) Ti–45Ni–5ZrO_2 and (e,f,g) Ti–40Ni–10ZrO_2 composites at different sintering temperatures. (a,b,e) 850 ºC, (c,f) 900 ºC and (d,g) 950 ºC.

Fig. 4. SEM images and EDS profile of spark plasma sintered Ti-Ni-ZrO_2 composites showing the distribution of phases.

Fig. 5. XRD patterns of sintered cp-Ti and Ti-Ni-ZrO_2 samples.

Fig. 6. The average microhardness values of the sintered samples.