Effect of ZrO_2 addition on the dry sliding wear behavior of laser clad Ti6Al4V alloy

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The relationship between microstructure and wear behavior of Ti6Al4V alloy and three laser-clad composite coatings (TiNi, TiNi5ZrO_2, and TiNi10ZrO_2) was investigated. Dry sliding wear tests were carried out using a ball-on-disk wear tester under varying loads. WC was used as the counterface material. The results showed that additions of ZrO_2 refined the microstructure of TiNi from a dendritic to a flower-like microstructure. An improvement in the microindentation hardness value was also observed. Results indicated that the wear volume of clad TiNi alloy decreased with the addition of ZrO_2 particles. The microstructural changes due to ZrO_2 additions played a significant role in the wear performance of the clad TiNi alloy. Analysis of worn surfaces and wear debris indicated that the dominant wear mechanism for the Ti6Al4V alloy was adhesive wear with ploughing.

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1. Introduction

Engineering materials with improved surface properties have been attracting a lot of interest in recent times. This is because of the critical technological challenges encountered on material surfaces due to engineering components/parts being exposed to extremely harsh environmental conditions. Surface properties of such engineering components require some modification in order to ensure safe operations of the parts [1]. Surface modification techniques can be employed to either decrease friction coefficient or increase surface hardness by changing surface chemistry of materials whilst maintaining the core properties of the bulk material [2,3].

Ti6Al4V is the most widely used titanium alloy. The alloy has been widely utilized in aero engines and airframes manufacturing fields as a result of their outstanding properties which include high strength-to-density ratio, good chemical resistance, and relatively low densities [4,5]. Titanium alloys however, are rarely used in areas where wear resistance property is required. They have been reported to have poor tribo-characteristics including high friction coefficient, low adhesion, and fretting wear resistance [6–8]. Machine designers have tried to avoid its use in sliding systems, but there are times when this is impossible. For instance, titanium fasteners are usually used to assemble titanium components. The disassembly and reassembly of such fasteners creates tapped holes as a result of wearing of the fasteners. The tribology limitations can effectively be improved via surface coating modifications using titanium-based composites. For instance, strengthening titanium with ceramic particles such as ZrO_2 has the potential to enhance the mechanical properties titanium-based composites. ZrO_2 has superior thermal and mechanical properties, which are effective as thermal barrier functions. Additionally, ZrO_2 has high fracture toughness due to stress-induced transformation which can be used in enhancement of fracture toughness of other ceramics and ceramics matrix composites [9]. ZrO_2 has also been widely used in industries as engine components, cutting tools and biomedical implants [10]. However, there have been few reported studies on titanium-nickel-zirconia composite coatings [1]. Advancement of the development of TiNiZrO_2 composite coatings will widen titanium alloys applications in areas where corrosion, wear and tribocorrosion resistance properties are required. In this
present study, the effect of ZrO₂ addition on the dry sliding wear behavior of Ti6Al4V has been investigated.

2. Materials and method

Ti6Al4V plates (100 mm × 50 mm × 10 mm in size) were used as the substrate while Ti (99.9% pure – 88 µm), Ni (99.9% pure – 88 µm) and 8% yttria stabilized ZrO₂ (99.9% pure – 44 µm) powders, supplied by Industrial analytical Pty, South Africa, were used as coating materials in the present study. The morphology of the powders was examined with a field emission scanning electron microscopy (FESEM, JSM-7600F, Jeol, Japan) equipped with energy dispersive X-ray spectrometer (EDS). Fig. 1 shows the SEM morphology of the three as-received powders. The titanium powder is rounded and spherical in shape, typical of atomized powders, while nickel powder is agglomerated and sintered. ZrO₂ powder was produced using the sol–gel method.

The three powders were mixed using the Turbula Shaker Mixer T2F in various mass ratios (Ti50Ni, Ti45Ni5ZrO₂ and Ti40Ni10ZrO₂ in wt%). An optimum mixing speed of 49 rpm and mixing time of 8 h were used. A 250 ml cylindrical plastic vessel with a powder fill level of 50% was loaded axially, placed in the mixing chamber and subjected to translational and rotational motions. The mixing was carried out in a dry environment.

Laser cladding technique was employed to deposit mixed powders on the Ti6Al4V substrate using ytterbium laser system (YLS) of 2 kW maximum power. Before laser cladding, the substrates were sandblasted, washed, cleaned with acetone and dried in air. The processing parameters were: Laser power 900 W, scanning speed 0.4 m/min, powder feed rate 2 g/min, gas flow rate 6 L/min and beam spot size 4 mm. Microhardness profiles of the cross section were measured using an EmcoTEST DuraScan microhardness tester at a load of 0.98 N (100 gf) and dwelling time of 15 s. Five indentation tests were taken and the average value was calculated.

In order to study the tribological behavior of the coatings (TiNi, TiNi5ZrO₂ and TiNi10ZrO₂), reciprocating–sliding friction tests were conducted using a CETR UMT-2 (Bruker Nano Inc., Campbell, CA) tribometer in a ball-on-disc configuration under ambient temperature. The schematic diagram of the tribometer setup is shown in Fig. 2. The test method involved the use of a WC counterface ball sliding against the specimen in a reciprocating motion under different loads of 5, 15, 25 and 35 N and at a frequency of 5 Hz. Each test was repeated three times for each set of conditions and the average value was taken for the calculation of wear volume. The loads on the specimens were applied vertically downwards with a motor-driven carriage that uses a load sensor for feedback to maintain a constant applied load. The dynamic normal load (FZ), friction force (Fx), depth of wear track (Z), and coefficient of friction (µ) were obtained from the UMT-2 tribometer software.

The single-trace analysis method was used to determine the wear volume on the scar surface [11]. This method requires only the scar size measurement and a single profiling trace on the scar surface. The single-trace analysis has shown good agreement with the 3D analysis and much higher accuracy than the mass loss and 2D analysis methods. Fig. 3 shows a schematic diagram of the wear scar obtained during the wear test for all the specimens. The wear volume of the flat specimen can be calculated by

\[
V_w = Ls \left[ R_s^2 \sin^{-1}\left(\frac{W}{2R_s}\right) - \frac{W}{2} (R_s - z_w) \right] + \frac{\pi}{3} z_w^2 (3R_s - z_w)
\]

where \( z_w \) is the wear depth, \( R_s \) is the radius of the spherical surface at both ends, \( W \) the width of the wear scar and \( V_w \) and \( Ls \) are the wear volume and Stroke length respectively.
3. Results and discussion

3.1. Microstructure and Microhardness

Fig. 4 shows the SEM micrographs of the Ti6Al4V substrate, laser-clad TiNi and TiNiZrO2 composites. Fig. 4a shows the typical two-phase structure of the Ti6Al4V alloy [12,13]. The inclusion of aluminum helped to stabilize the alpha phase while vanadium stabilized the beta phase [14]. The α-phase (the grey phase) has an HCP structure whereas the β-phase (white phase) has a BCC structure. From Fig. 4b and c, the coatings revealed flawless microstructures with no detection of pores or cracks. Fig. 4b shows the microstructure of laser-clad TiNi alloy which consist of a dense and uniformly distributed primary TiNi dendrites. Similar results was also reported by Gao and Wang [15]. SEM micrograph of the laser-clad TiNi coating with ZrO2 addition is shown in Fig. 4c. The microstructure consist of a flower-like structure and homogeneously distributed three distinct phases as confirmed with EDS; Ni-rich phase (grey), ZrO2-rich phase (white) in a matrix of Ti-rich phase (dark). Obadele et. al [1], reported that ZrO2 addition improve the microstructure of TiNi coatings.

Microhardness profiles along the clad surface to the substrate of the coatings are shown in Fig. 5. The values were obtained by making five indentations at 100 mm interval and the average value calculated. The hardness value of the Ti6Al4V substrate was relatively constant at 338 HV0.1. The microhardness value of TiNi is about 696 HV0.1 while that of TiNi5ZrO2 and TiNi10ZrO2 are approximately 1048 and 1172 HV0.1 respectively. The increase in hardness value is as a result of ZrO2 phase present in the composite matrix.

3.2. Wear study

3.2.1. Wear volume and friction coefficient

In order to compare wear data for all the samples, wear volume was calculated by measuring the width of the wear scar (transverse to the sliding direction) and the wear depth obtained from the UMT-2 software according to the equation formulated by Qu and Truhan [11]. The calculated cumulative volume loss versus different loads (5, 15, 25 and 35 N) curves are shown in Fig. 6. It can be found that the weight loss of Ti6Al4V increases almost linearly as the contact load increases from 5 to 25 N. However, a slight increase in gradient was observed at an applied load of 35 N which suggest the coarser worn surface when compared with the laser clad composites. This shows a gradual transformation from mild wear to severe wear at higher loads. Molinari [16] suggested that the poor tribological properties titanium alloys can be attributed to two main factors; the low work-hardening and low plastic shearing resistance, and also, the low protection exerted by the surface oxide due to high flash temperatures induced by friction during the dry sliding process.
Wear volume losses of TiNi samples with and without ZrO2 are also presented in Fig. 6. With increasing ZrO2 addition, wear volume loss decreases significantly. This improvement in wear resistance can be attributed to the presence of ZrO2 phases which also caused an increase in hardness values. A strong effect of ZrO2 addition on the wear resistance property of TiNi is noticeable under 5 N applied load. Under high loads, for TiNi without ZrO2, there could be loss of pseudoelasticity, since under high stresses, frictional heat is increased and dislocation can be generated [17].

Fig. 7 shows the variation of friction coefficient with sliding time at different loads of 5, 15, 25 and 35 N under dry conditions respectively. As it can be seen, the friction coefficient of TiNi with ZrO2 is lower than that of TiNi without ZrO2. At the initial stage under 5 N load, the variation of steady state friction coefficient for TiNi10ZrO2 is the lowest at 0.1 which confirms the least volume loss in Fig. 6. Generally, the friction coefficient of metals/alloys are usually higher than hard materials like ceramics. The steady state friction coefficient of TiNi with ZrO2 addition was relatively maintained below 0.4 and that without ZrO2 addition was above 0.4. This indicates that TiNi coatings with ZrO2 addition possess better wear resistant than TiNi coatings without ZrO2.

3.2.2 Wear scar morphology and wear debris

Fig. 8 indicates the SEM images of the worn and unworn regions on the Ti6Al4V alloy and TiNi10ZrO2 composites specimen under applied load of 35 N. It could be seen that Ti6Al4V alloy has a coarser than that of TiNi10ZrO2 (Fig. 8b) under the same applied load. Parallel ploughs in the sliding direction and also features of compact oxide debris layer and detachment could be clearly observed within the wear scar (Fig. 8c). This could probably indicate that the Ti6Al4V surface underwent significant abrasive wear under reciprocating sliding condition.

Fig. 8b and d shows that TiNiZrO2 composite produced abrasive depth that is relatively shallow with non-continuous wear grooves. This worn surface could be attributed to the uniform dispersion and high adhesion strength [18] of ZrO2 phase as well as the bonding strength between TiNi and ZrO2 in the laser clad composite coating, thus creating high wear resistance under dry condition.
Wear debris of the Ti6Al4V alloy under a test load of 35 N comprised loose tiny powder debris and mostly consists of flake-like chips, as indicated in Fig. 9a. EDS analysis of the wear debris reveal that the powder debris and most of the flake-like chips are Ti-rich with trace amount of Al. This indicates that the wear debris were from the Ti6Al4V substrate with no trace of elements from the counterface WC ball. The wear debris of laser-clad TiNiZrO2 consist of mostly powder debris with fewer flake-like chips (Fig. 9b) of Ti which suggest that the coating underwent less severe wear. The size of flake-like wear debris could be related with the severity of adhesive wear [19]. The significant reduction in the Ti-rich flake-like chips could be as a result of the adhesion strength offered by the ZrO2 particles within the matrix of TiNi composites, excellent mechanical strength and toughness of ZrO2 particles, and enhanced resistance to plastic deformation (higher hardness as shown in Fig. 5) as compared with Ti6Al4 V alloy and TiNi composite coating.

4. Conclusion

The dry sliding wear behavior of titanium composite has been investigated. The main conclusions are:

1. The addition of ZrO2 reinforced particles refined the microstructure of TiNi from dendritic to flower-like structure.
2. The TiNiZrO2 composite coatings exhibited higher hardness, lower friction coefficient, and better wear resistance than that of Ti6Al4V alloy and laser-clad TiNi composite prepared under the same laser surface cladding conditions.
3. The addition of ZrO2 acted as reinforeacement in the titanium matrix to reduce the friction coefficient even at a much higher load and hence improved the wear properties.
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