Atmosphere Gas Carburizing for Improved Wear Resistance of Pure Titanium Fabricated by Additive Manufacturing

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In order to improve wear resistance of pure titanium fabricated by additive manufacturing, its surface was hardened by atmosphere gas carburizing. For the study, the pure titanium was fabricated by electron beam melting system. The microstructures and wear properties of the as-built and carburized titanium were investigated. After carburizing, hardness was increased and titanium carbides were precipitated in the surface region. The friction coefficients of the both specimens were estimated by dry sliding friction tests; the friction coefficient of carburized titanium is lower than that of as-built titanium. The improvement of wear property would be a result of high surface hardness and the slippery nature of titanium carbide formed on the surface.

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1. Introduction

Additive manufacturing (AM) is a new technology in which products are fabricated by adding material in a layer-by-layer fashion¹. This makes it possible to create products with a mesh structure or complex internal structure that would not be possible using conventional methods, which has resulted in AM receiving a lot of attention recently. Indeed, the popularity of this technology has already seen its use expanding from polymers to metallic materials²³. Titanium (Ti) is widely used in the chemical and aerospace industries due to its high corrosion resistance and strength to weight ratio⁴. It has also been receiving attention as a biomaterial for in vivo implants and surgical equipment because of its good bio-compatibility when compared to other metallic materials⁵. Unfortunately, Ti is also well known for its poor wear properties (i.e., a low hardness and high friction coefficient)⁶, which greatly limits its usefulness in many engineering applications.

In addition, its limited number of slip systems as well as a low modulus of elasticity and low thermal conductivity result in poor formability and machinability⁷. This makes it difficult to manufacture Ti products with complex three-dimensional (3D) structures using conventional methods, but such products can be achieved with AM technology. Furthermore, commercially pure Ti fabricated by AM technology, typically has a higher strength and hardness due to the residual stress induced by the process⁸⁹. Despite these improved mechanical properties, surface hardening may still be needed to provide sufficient wear resistance in industrial applications.

Various surface modification techniques have been developed to improve the wear resistance of Ti, such as carburizing, nitriding, and oxidation¹⁰⁻¹³. Of these, atmosphere gas carburizing has been the most widely used in many industries due to its low cost and the uniformity of the results it achieves. This improves the wear resistance of Ti by creating a surface layer of Ti carbide particles with a high hardness and low coefficient of friction; however, there has been no research into the application of this process to Ti products fabricated by AM technology. This study therefore looks at the effects of atmosphere gas carburizing on the microstructure and wear properties of pure Ti products fabricated by AM through surface hardness and friction coefficient measurements.

2. Experimental Procedure

Grade-2 Ti powder (O < 0.25 mass%) with an average particle diameter of 70 μm was used as the starting material for additive manufacturing. A pure-Ti bulk specimen was fabricated to a size of 150 × 70 × 10 mm, as shown in Fig. 1, using an electron beam melting system (A2X, ARCAM) with an electron beam power of 240–1800 W and a scanning speed of ~1000 mm/s. The oxygen and nitrogen concentrations of the as-built titanium specimen were determined using an oxygen/nitrogen analyzer (ONH836, LECO) to be 0.189 and 0.021 mass%, respectively, with both values satisfying the Grade-2 standard for Ti. For carburizing and wear resistance testing, the bulk sample was machined into disks with a diameter of 30 mm and thickness of 5 mm.

The disk-shaped Ti specimens were subjected to atmosphere gas carburizing via the process schedule outlined in
Fig. 2. For carburizing, 40% nitrogen (N₂, purity > 99.99%) - 60% methanol (CH₃OH, purity > 99.99%) gas mixture was used as a carrier gas and propane (C₃H₈, purity > 99.99%) was used as an enriching gas. This entailed heating the specimen to 920°C for 2 h, and then carburizing it for 4 h at a carbon potential of 1.1%. The carbon potential was then lowered to 0.8% to allow carbon to diffuse from the surface to the interior of the specimen, after which the specimens were quenched in hot oil at 120°C. After carburizing, the surface of the specimen was removed through polishing to a depth of 50 μm to eliminate any oxide layer formed during carburizing, as this is known to have a harmful effect on the wear properties of Ti due to its sudden failure and cracking even at relatively low loads (14). The microstructures of the as-built and carburized Ti specimens were then observed at both their surface and center. To estimate the change in hardness as a result of carburizing, micro Vickers hardness testing was carried out from the surface to the center of each sample using a step size of 100 μm (AAV-503M, Mitutoyo).

To examine the formation of carbides due to carburizing, the surfaces of the as-built and carburized Ti specimens were examined by X-ray diffractometry (Empyrean, PANalytical) using Cu Kα radiation. The carburized Ti specimen was also analyzed by transmission electron microscopy (TEM) (JEM-2100F, JEOL) to confirm the existence of carbide. For TEM observation, a sample was prepared by a method of carbon extraction replica (15). Chemical composition of surface layer precipitate was investigated using an energy dispersive X-ray spectroscopy (X-Mız, Oxford) with TEM according to the Cliff-Lorimer method.

In order to estimate the wear resistance of the as-built and carburized Ti specimens, dry sliding friction wear tests were carried out using a pin-on-disk tribometer (Micro-tribometer, CSEM Instruments). To compare the wear resistance of commercially produced pure Ti and as-built Ti, the wear resistance of commercially produced pure Ti (Grade 2) sheet was also examined using the tribometer. A bearing steel (commercial SAE 52100 grade) ball with a diameter of 8 mm was used as a pin, to which a 10 N load was applied during testing. This pin was swept over a diameter of circular rotation of 10 mm at a rotational speed of 200 rpm for a total operating time of 3600 s. The friction coefficient was recorded continuously during testing via a computerized data recording system. The change in mass of as built and carburized Ti specimens after testing was measured to estimate their wear resistance.

3. Results and Discussion

The optical microscope images in Fig. 3(a) and (b) show the microstructures of the as-built and carburized Ti specimen, respectively, as observed in a direction perpendicular to the building direction. Note that with both specimens the microstructure at the surface is similar to that at the center, but the grains in the as-built Ti specimen grew along the build direction to produce an elongated, columnar grain structure typical of metallic materials fabricated by AM (9,16). After carburizing, however, the microstructure was drastically altered to one of needle-shaped grains.

To examine the hardness change by carburizing, micro Vickers hardness tests of the both specimens were performed. Hardness values were measured from the surface to the center with a step size of 100 μm and the results are shown in Fig. 4. The hardness of the as-built Ti was the same at its surface as at the center, with an average value of 222 HV. This is notably higher than the Vickers hardness of commercially pure Grade-2 Ti fabricated by conventional methods, which is typically around 170–200 HV (17). The reason for this is that a cyclic thermal shock is produced during AM by the Ti powder being melted by the electron beam and then rapidly cooled (18). This, in turn, produces residual stress and increases the hardness of pure Ti. Following carburization, the hardness at the surface is increased to 432 HV, but gradually decreases to...
287 HV at the center. Note that as this is still higher than the hardness of the as-built Ti, some carbon would diffuse all the way to the center during carburizing.

Concentration of carbon in titanium severely affects the hardness of pure Ti and its alloy. When carbon is dissolved as an interstitial atom in Ti, it can drastically increase the hardness of the metal through solid solution strengthening. Furthermore, as the solubility limit of carbon in the $\alpha$-Ti matrix is only about 0.2 mass\%, any excess carbon beyond this is precipitated in the form of carbides that also increase the hardness of Ti.

To determine whether Ti carbides were formed as a result of carburization, the as-built and carburized specimens were subjected to XRD analysis. Figure 5 shows the XRD results of the both specimens. $\alpha$-Ti phase was found to be present in the both specimen, but a minor peak was also detected at a 2\theta angle of around 60° in the carburized Ti specimen. Subsequent measurements were therefore made in the 52° to 68° 2\theta range, which confirmed that a peak appears at 60.5° after carburizing, that is indexed to TiC.

To further confirm the presence of TiC, the surface of the carburized Ti specimen was observed by TEM. As shown in the bright-field TEM image and selected area diffraction pattern in Fig. 6, nano-sized precipitates were formed in the carburized Ti specimen that were identified as TiC (JCPDS 98-015-9871, Cubic, Fm$3m$, $a = 4.3250$) with a zone axis in the [001] direction. The chemical composition of this precipitate, as shown in Table 1, was also consistent with TiC.

To investigate the improvement of wear resistance of the as-built Ti by atmosphere gas carburizing, dry sliding friction tests were carried out using a pin-on-disk tribometer. Figure 7 is the friction coefficient curves of the commercially produced pure Ti (Grade 2) sheet, as-built Ti, and carburized Ti specimen. The average friction coefficient of commercially produced pure Ti (Grade 2) sheet and as-built Ti specimen
was 0.621 and 0.592, respectively. Vickers hardness of commercially pure Grade-2 Ti fabricated by conventional methods is typically around 170–200 HV\(^1\)) and it of the Ti sheet used in this study was 187 HV, which value is lower than the hardness of as-built Ti (222 HV). During AM, residual stress is produced by a cyclic thermal shock, which would result in the increase of hardness and decrease of friction coefficient.

The carburized Ti specimen had a lower average friction coefficient (0.406) than the as-built Ti specimen (0.592). It would therefore seem that carburizing treatment reduces the friction coefficient of Ti by one-third. The change in mass before and after wear resistance testing presented in Table 2 reveals that the as-built Ti lost 47.7 mg, whereas the mass of the carburized Ti only decreased by 36.9 mg. This indicates that the wear resistance of Ti fabricated by AM can be improved by carburizing. During carburizing, carbon is diffused to Ti and dissolves as an interstitial atom in the Ti matrix until the solubility limit of 0.2 mass%. As carbon content is increased, the hardness of Ti is drastically increased by solid solution strengthening\(^{19}\), which would result in the decrease of friction coefficient and increase of wear resistance. The improved wear resistance would also result in the precipitation of TiC particles that have a low friction coefficient\(^{14}\), which helps to create a slippery surface on the carburized Ti specimen.

4. Conclusions

The wear resistance of commercially pure titanium metal fabricated by AM has been successfully improved through atmosphere gas carburizing. This has been shown to increase the surface hardness from 222 to 432 HV and produce TiC particles on the product surface through the diffusion of carbon. As a result of this, the friction coefficient is reduced by one-third from 0.592 to 0.406, resulting in a significant decrease in the weight that is lost during wear resistance testing.

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