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Carbide layer coating on titanium by spark plasma sintering technique

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ABSTRACT

Titanium materials are widely used in aerospace, automotive and biomaterial engineering fields due to high specific strength, superior fatigue and corrosion resistance as well as excellent biocompatibility. However, titanium exhibits low hardness and poor wear resistance. Therefore, the development of a suitable surface modification technology is necessary to expand the use of titanium materials. In order to improve hardness and wear resistance of materials, there is the method to form the hard ceramics layer on the matrix surface. In this study, carburizing method was applied. The carburizing method can form the carbide layer which is superior in adhesion with the matrix compared with PVD or CVD method. However, in conventional carburizing methods, the deterioration of the mechanical properties of the matrix as a result of long-term and high-temperature processing is problematic. Therefore, spark plasma sintering technique, which features short processing times, was applied to form a carbide layer in this study. The purpose of this research is to form a TiC layer on commercially pure Ti (CP-Ti) and evaluate its properties. CP-Ti was used as the substrate, and graphite powder was used as the carburizing source. XRD analyses indicated that a TiC layer was formed on the substrates. Corrosion tests indicated that the corrosion resistance of the carburized samples was remarkably improved compared to that of CP-Ti. Wear tests revealed that the carburized samples exhibited low friction coefficients and improved tribological properties.

1. Introduction

Titanium materials are widely used in the aerospace, chemical, automotive, and biomaterial engineering fields because of their high specific strength, superior fatigue and corrosion resistance, and excellent biocompatibility. However, titanium exhibits poor wear resistance because of its high friction coefficient and low hardness. Therefore, a surface modification technology that maintains titanium's properties is needed to expand the use of titanium materials.

Methods have been developed to form a hard-ceramic layer on the matrix surface of materials to improve their hardness and wear resistance [1–3]. In the case of titanium-based materials, a TiC layer is often formed via chemical vapor deposition (CVD) or physical vapor deposition (PVD) [3,4]. Titanium carbides exhibit high melting points, high hardness and good wear resistance. However, TiC coating layers formed by CVD or PVD do not exhibit good adhesion to their substrates; this poor adhesion has been reported to lead to exfoliation and fracture at the substrate-coating layer interface [5,6]. In contrast, the carburizing method is expected to form a carbide layer with matrix adhesion superior to that of carbide layers deposited via PVD or CVD. However, in conventional carburizing, the mechanical properties of the matrix can deteriorate under extended high-temperature processing. Therefore, in the present study, the spark plasma sintering (SPS) technique, which can be used to treat materials with a short processing time [7], was applied to form ceramic layers.

Recently, the utility of SPS has been demonstrated in ceramic/metal nano-materials, composites materials system functionally graded materials (FGMs), hard materials, electronic materials, thermoelectric conversion materials, and biomaterials [8–13]. In this technique, raw material powder is packed into a graphite die, to which a pulse current is subsequently applied while the die is maintained under uniaxial pressure. This process leads to Joule heating among powder particles, which promotes sintering. This method was also used for the joining of dissimilar ceramics and/or metals [14–19] and coating [20–28]. The fabrication of carbide [20], boride [21], silicide [22], ceramics [23,24], composites [25–27], and high entropy alloy coatings [28] on metal or ceramics substrate has also been achieved using SPS. The coatings fabricated using SPS demonstrated strong metallurgical bonding between the coating and substrate. In this study, commercially pure Ti (CP-Ti) was used as a substrate and graphite powder was used as the carburizing source. The advantages of the SPS technique include its moderate uniaxial pressure and shorter sintering time compared to

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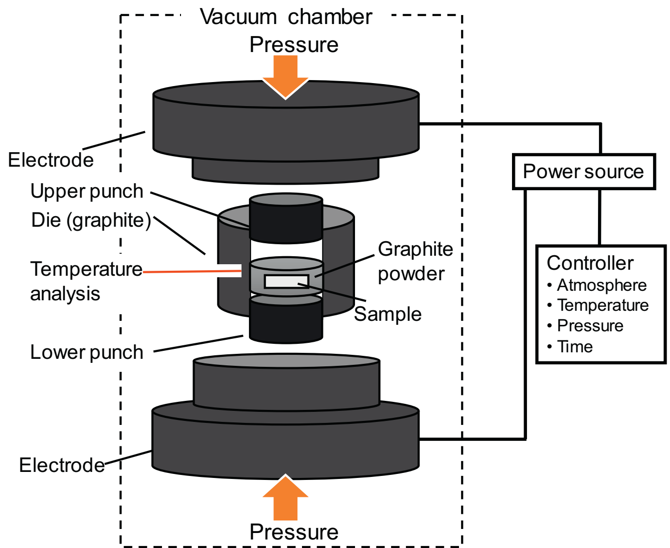

Fig. 1. Schematic illustration of the setup for CP-Ti sample and graphite powder in a graphite die for SPS.

those used in traditional methods, in addition, the applied pulse current may facilitate the diffusion of carbon atoms.

2. Experimental details

CP-Ti (purity 99.5%) was used as the substrate, and graphite powder (particle size 45 μm, purity 98.0%) was used as the carburizing source. The square plate sample ($10 \times 10 \times 1\ mm^3$) for corrosion test and disk sample (ϕ20 mm × 5 mm) were wet polished to #2000. Raw material powders were filled into a BN-coated cylindrical graphite die with an inner diameter of 20 mm. The polished substrate was first inserted into the powder, followed by the insertion of a graphite punch. The sample was coated using an SPS system (model SPS-1020, produced by Sumitomo Coal Mining Co., Japan) under a uniaxial pressure of 11 MPa and a vacuum lower than 10 Pa. Fig. 1 shows schematics of the SPS setup. The heating time was 0.6 ks, the coating time was 3.6 ks, and the coating temperature was 1143, 1243, and 1343 K. The sample temperature was measured using a thermocouple in the case of coating temperatures of 1143 K and 1243 K and using a radiation thermometer in the case of coating temperature of 1343 K. After coating, the sample was cooled to room temperature by furnace cooling. Fig. 2 shows the temperature program.

After coating, to identify the phases, we analyzed the sample surface by θ–2θ X-ray diffraction (XRD; RINT-2550V, RIGAKU, Tokyo, Japan) at room temperature in the range $20° \leq 2\theta \leq 90°$. The X-ray diffractometer was equipped with a Cu-Kα radiation source operated at 40.0 kV and 300 mA, the samples were scanned at 40.0°/min.

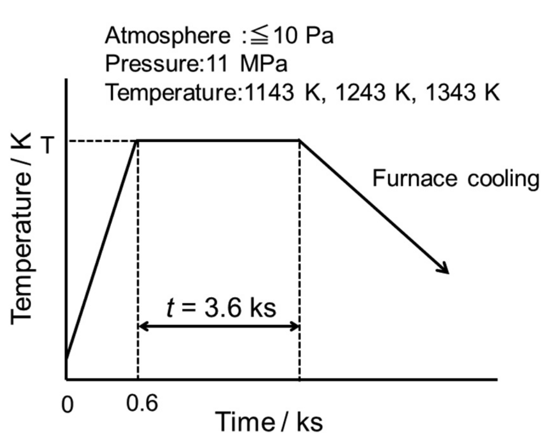

Fig. 2. The temperature program during SPS carburizing.

To investigate the corrosion resistance, we immersed the square plate samples in 2% HF–10% HNO_3 solution and measured the decrease in weight after 10 min. The microstructure of the samples was characterized by scanning electron microscopy (SEM, JEOL, JSM-6060LV) and energy-dispersive X-ray spectrometry (EDX). Depth chemical profiles and element contents were obtained using glow-discharge optical emission spectroscopy (GD-OES, HORIBA, GD-Profiler2). The GD-OES conditions were a sputtering-mark diameter of 4 mm, a discharge pressure of 600 Pa, and a power of 35 W.

The tribological performance of the sample was evaluated using a ball-on-disc tribometer (CSM Instruments, Tribometer, Switzerland). The tests were carried out under air atmosphere, with a sliding speed of 100 rpm, a wear-track radius of 5 mm, a sliding distance of 500 m, and a load of 2 N; Al_2O_3 balls with a diameter of 6.00 mm were used as the counter material. The surface hardness was measured using a Vickers microhardness tester (PMT-X7A, Matsuzawa, Akita, Japan) under a load of 0.25 N maintained for 10 s. The reported hardness values are the average results obtained for five measurements.

3. Results and discussion

Fig. 3 shows XRD patterns of samples subjected to different carburizing temperatures. The current composites mainly consist of α-Ti phase and TiC phase, irrespective of the treatment conditions. The intensity of TiC phase increased with an increase of carburizing temperature. And impurities peaks associated with, for example, oxides were not detected. The lack of impurities is attributable to the carburizing treatment being conducted under vacuum, the carbon reduction effect stemming from the use of a graphite die, and the oxide film on the CP-Ti substrate being broken by the high-temperature plasma generated by the pulse current. Oxygen atoms have been reported to inhibit carbon diffusion into TiC layers, thus, to increase the thickness of the TiC layer, removal of oxygen is important [29]. In this study, the spark plasma sintering method effectively grew the TiC layer. In the XRD patterns, peaks associated with graphite were also intense. Fig. 4 shows the results of SEM-EDX analysis of the sample surface after carburizing treatment for 3.6 ks at 1343 K by SPS; particles similar to the raw powder are observed. We attributed the graphite peaks in the XRD pattern to graphite powder from the carburizing source. These results indicate that the SPS carburizing technique resulted in the formation of a TiC layer on the Ti substrate via treatment for 3.6 ks.

Fig. 5 shows the test results for samples corroded using 2% HF–10% HNO_3 solution. The weight loss per unit surface area is shown as a function of the immersion time. In this study, the weight loss is calculated for a surface area of $240\ mm^2$. The samples carburized by SPS exhibited improved corrosion resistance compared to the substrate because of the formation of a TiC layer, which exhibits corrosion

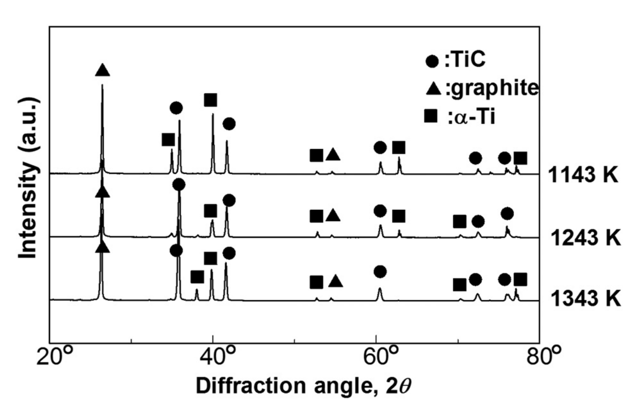

Fig. 3. XRD patterns of samples subjected to SPS carburizing treatment.