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Surface strengthening of Ti_3SiC_2 through magnetron sputtering Cu and subsequent annealing

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Abstract

Magnetron sputtering deposition Cu and subsequent annealing in the temperature range of 900–1100 °C for 30–60 min were conducted with the motivation to modify the surface hardness of Ti_3SiC_2. Owing to the formation of TiC following the reaction $Ti_3SiC_2 + 3Cu \rightarrow 3TiC_{0.67} + Cu_3Si$, the surface hardness was enhanced from 5.08 GPa to a maximum 9.65 GPa. In addition, the surface hardness was dependent on the relative amount of TiC, which was related to Cu film thickness, heat treatment temperatures and durations of annealing. Furthermore, after annealing at 1000 °C for 30 min the Cu-coated Ti_3SiC_2 has lower wear rate and lower COF at the running-in stage compared with Ti_3SiC_2 substrate. The reaction was triggered by the inward diffusion of Cu along the grain boundaries and defects of Ti_3SiC_2. At low temperature and short annealing time, i.e. 900 or 1000 °C for 30 min, Cu diffused inward Ti_3SiC_2 and accumulated at the trigonal junctions first. At higher temperature of 1100 °C or prolonging the annealing time to 60 min, considerable amount of Cu diffused to Ti_3SiC_2 and filled up the grain boundaries leaving a mesh structure.

Keywords: Ti_3SiC_2; Surface strengthening; Magnetron sputtering; Microhardness; Tribological property

1. Introduction

In recent years, layered ternary carbides and nitrides, such as Ti_3SiC_2, Ti_3AlC_2, Ti_2AlC, Ti_2SnC and Ti_2AlN, are attracting much attention owing to their unique combination of properties of both metals and ceramics. They have been recognized as materials for potential applications in various industrial fields. Among all these compounds, Ti_3SiC_2 has been most extensively investigated. It has low density, good thermal and electrical conductivity, high elastic moduli and easy machinability.[1–4] However, compared with traditional binary carbides, for instance TiC, its hardness and wear resistance are relatively low, which limit its widespread applications. Therefore, surface strengthening to modify the properties of Ti_3SiC_2 without losing its intrinsic merits is of vital importance.

In order to enhance the surface hardness of Ti_3SiC_2, El-Raghy and Barsoum[5] altered its surface chemistry through two ways: carburization and silicidation. Reaction of Ti_3SiC_2 with graphite foils in the temperature range of 1400–1600 °C resulted in the formation of a 15 vol.% porous surface layer of TiC_x (where $x > 0.8$), which increased the surface hardness from 4 to 20–25 GPa. While in the process of silicidation, reaction of Ti_3SiC_2 with silicon wafers in the temperature range of 1200–1350 °C resulted in the formation of a dense surface layer composed of a two-phase mixture of $TiSi_2$ and SiC, which also increased the surface hardness to 10–12 GPa. Li et al.[6] improved the surface hardness and wear resistance of Ti_3SiC_2 by boronizing treatment, which was carried out through powder pack cementation in the temperature range of 1100–1400 °C. A maximal hardness of 9.3 GPa was obtained with the formation of a layer of TiB_2 and β-SiC mixture, meanwhile its wear resistance was also significantly improved.

It is well known that the crystal structure of Ti_3SiC_2 can be considered as two-dimensional closed packed layers of Si periodically intercalated into the (1 1 1) twin boundary of $TiC_{0.67}$ (Ti_3C_2).[7] The de-intercalation of Si from Ti_3SiC_2 caused the

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topological transformation from hexagonal Ti_3SiC_2 to cubic $TiC_{0.67}$. Obviously, when the de-intercalation takes place, the as-formed TiC will increase the hardness of Ti_3SiC_2. Thus the motivation for this work is to induce the topological transformation at the surface of Ti_3SiC_2, which could take place when it contacts in Cu,[8] Ni,[9] graphite,[5] molten cryolite[10] and liquid Al.[11] Since Cu films can be deposited readily by magnetron sputtering, which is a well-established technology with lower working gas pressure and higher sputtering rate,[12] in the present work, to enhance the surface hardness and wear resistance, a thin layer of Cu was deposited on Ti_3SiC_2 followed by annealing at high temperature. In addition, the reaction products, microstructure, Vickers hardness and tribological properties of the reaction layer were investigated.

2. Experimental procedures

2.1. Substrate material

The bulk Ti_3SiC_2 used in this work was fabricated by an in situ hot pressing/solid–liquid reaction process, which was described in detail elsewhere.[3] The measured density of Ti_3SiC_2 was 97% of the theoretical value, which was determined by the Archimedes' immersion method. The Ti_3SiC_2 substrate was cut into rectangular specimens of 8 mm × 8 mm × 2 mm by electrical discharge method from an as-fabricated bulk piece. The surfaces used for sputter deposition were ground down to 1500 grade SiC paper, mechanically polished using 1.5 μm diamond paste to ensure a flat and mirror-like surface, and then ultrasonically cleaned in ethanol and acetone individually for 10 min before they were transferred into the sputter chamber.

2.2. Deposition of Cu

A JGP560C14 ultrahigh vacuum (UHV) magnetron sputtering deposition system (SKY Technology Development Co. Ltd, Shenyang, China) was used in depositing polycrystalline Cu films onto Ti_3SiC_2 substrate. A schematic diagram of a direct current (dc) magnetron sputtering system used in the present work is shown in Fig. 1. Copper target of 99.99% purity with 60 mm in diameter was used. During deposition, the substrates were kept static with the substrate-to-target separation (d_{s-t}) of 60 mm to ensure an identical condition for each run. The sputtering chamber was evacuated to a base pressure of $\sim 5 \times 10^{-4}$ Pa, and then backfilled with high purity argon to the required coating pressure at 0.4–0.5 Pa with a gas flow rate of generally 20 sccm. Cu film deposition process was carried out under the dc power of 100 W, meanwhile a negative dc bias of 100 V was applied to the substrate. The detailed process parameters are listed in Table 1. Prior to deposition, the pure copper target was pre-sputtered for 5 min in order to remove the contaminants and oxides on the surface. During the target cleaning, a shield was interposed between the target and the substrate to avoid the substrate contamination. Although there was no deliberate attempt at heating the substrates, the temperature of the films rose as high as ~70 °C during magnetron sputtering as a result of the condensing of the sputtered atoms—the heat of condensation plus their kinetic energy.

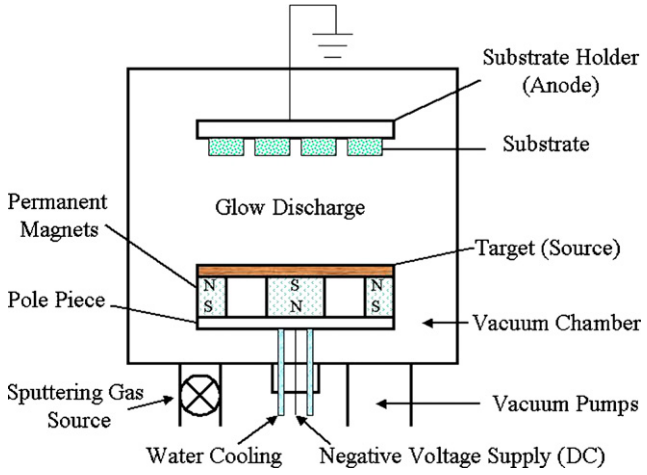

Fig. 1. Schematic illustration of a magnetron sputtering system.

2.3. Annealing process

After deposition, the Cu-coated Ti_3SiC_2 samples were annealed in order to obtain a layer composed of TiC and copper silicides. There was no apparent reaction between Ti_3SiC_2 and Cu at temperatures below 900 °C, according to previous work on high-temperature reaction between Ti_3SiC_2 and Cu by Zhou et al.[8] Thus, attention was only paid to the samples annealed at temperatures above 900 °C. In this work, Cu-coated Ti_3SiC_2 were annealed at various temperatures ranging from 900 to 1100 °C for 30–60 min in a horizontal tube furnace under flowing argon atmosphere. The detailed process parameters are listed in Table 2.

Table 1
Parameters for the deposition of Cu on Ti_3SiC_2 by magnetron sputtering method

Target source	Cu (diameter: 60 mm)
Substrate	Ti_3SiC_2 (dimension: 8 mm × 8 mm × 2 mm)
Sputtering gas	Ar
Base pressure (Pa)	5×10^{-4}
Gas partial pressure (Pa)	0.4–0.5
Gas flow rate (sccm)	20
dc sputtering power (W)	100
Negative dc bias applied to the substrate (V)	100
Substrate temperature[a] (°C)	70
Substrate-target distance (mm)	60
Deposition time (h)	2~6
Deposition rate (μm/min)[b]	0.17

[a] Although there was no deliberate attempt at heating the substrates, the temperature of the films rose as high as ~70 °C during magnetron sputtering as a result of the condensing of the sputtered atoms—the heat of condensation plus their kinetic energy.

[b] The thickness of the film is measured using a HXD-1000B digital microhardness tester and the growth rate is calculated from the film thickness obtained for a given deposition time.