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ScienceDirect

Surface & Coatings Technology 201 (2007) 6005–6011

SURFACE & COATINGS TECHNOLOGY

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Improving the surface hardness and wear resistance of Ti_3SiC_2 by boronizing treatment

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Received 6 August 2006; accepted in revised form 11 November 2006
Available online 21 December 2006

Abstract

In order to modify surface properties of Ti_3SiC_2, boronizing was carried out through powder pack cementation in the 1100–1400 °C temperature range. After boronizing treatment, one mixture layer, composed of TiB_2 and β-SiC, forms on the surface of Ti_3SiC_2. The growth of the coating is processed by inward diffusion of boron and obeys a linear rule. The boronizing increases the hardness of Ti_3SiC_2 from 3.7 GPa to a maximal 9.3 GPa and also significantly improves its wear resistance.

Keywords: Boronizing; Ti_3SiC_2; Diffusion coatings; Hardness; Wear resistance

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1. Introduction

Layered ternary carbides, such as Ti_3SiC_2, Ti_3AlC_2 etc., possess an unusual combination of the merits of metals and ceramics, including low density, high modulus and strength, high electrical and thermal conductivity, good thermal stability and machinability [1–5]. Therefore, these materials are of great interest for potential applications in many industrial fields. Especially, Ti_3SiC_2 has been considered as high temperature structural component due to its superior mechanical properties. However, compared with traditional binary carbides, its hardness and wear resistance are relatively low. In order to enhance these properties without losing its initial merits, surface modifications or the application of hard coatings are effective ways.

To modify the surface hardness of Ti_3SiC_2, EL-Raghy and Barsoum [6] prepared carburized layer on Ti_3SiC_2 by setting up diffusion couples between graphite foils and the Ti_3SiC_2 coupons and treating the sandwich thermally in vacuum of about 1 MPa dead load. In the 1400–1600 °C temperature range, reaction of Ti_3SiC_2 with graphite foils resulted in the formation of a single phase layer of TiC_x (where $x > 0.8$) with porosity of about 15 vol.%. It was shown that the carburization of Ti_3SiC_2 increased its hardness from 4 GPa to 20–25 GPa. Meanwhile, they used the same method but replacing graphite foils with silicon wafers to perform silicidation of Ti_3SiC_2, the high temperature oxidation resistance of Ti_3SiC_2 was raised by about three orders of magnitude after the silicidation treatment.

It is well known that titanium diboride exhibits high hardness and excellent wear resistance in many tribological systems. Since Ti_3SiC_2 contains significant amounts of titanium, titanium diboride is expected to form on its surface during boronizing treatment, subsequently the surface hardness and wear resistance of Ti_3SiC_2 can be improved. In fact, boronizing is widely used as a thermochemical surface hardening treatment method for metals and alloys [7]. Depending on physical state of boronizing media, various boronizing methods have been developed [8]. Among them, powder pack cementation is most commonly used because of its simpleness, practicality and low cost. Apart from metals and alloys, boronizing has also been successfully applied to modify the properties of some sintered carbides [9–11]. However, boronizing of Ti_3SiC_2 or other layered ternary carbides has not been reported.

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doi:10.1016/j.surfcoat.2006.11.008

In the present work, in order to improve the surface hardness and wear resistance of Ti_3SiC_2 ceramic, boronizing was conducted by powder pack cementation. The optimal condition for boronizing of Ti_3SiC_2 was investigated. Based on the analysis of the composition, microstructure and growth kinetics of boronizing coatings, the forming mechanism of the coatings was discussed, and their surface hardness and wear properties were examined.

2. Experimental procedures

2.1. Substrate material and boronizing process

The Ti_3SiC_2 used in this work was fabricated by an *in situ* hot pressing/solid–liquid reaction process, the preparation steps have been described in detail in the previous work [12]. The measured density of the Ti_3SiC_2 used in this work was about 98% of the theoretical density determined by the Archimedes' method.

Ti_3SiC_2 coupons with dimensions of 5 mm × 5 mm × 2 mm were cut by an electrical discharge method from an as-fabricated bulk piece. The surfaces were ground down to 1000 grade SiC paper and polished using 1.5-μm diamond paste. The specimens were ultrasonically cleaned in acetone and distilled water before boronizing treatments.

Boronizing was performed by using a fluoride-activated powder pack cementation method. The boronizing media were composed of 50 wt.% B_4C (purity >85%; average particle size <200 mesh), 45 wt.% SiC (purity >98%; average particle size <400 mesh), 2 wt.% Si (purity >99%; average particle size <200 mesh) and 3 wt.% KBF_4 (analytical pure). In this boronizing media, B_4C serves as the source of boron, SiC as the diluent, Si as the reducing agent, and KBF_4 as the active agent. Briefly, the boronizing process was carried out in the following procedure: all the media powders were mixed in a polyurethane jar for 8 h, using stainless steel balls coated with a layer of polyurethane as the mixing medium; Ti_3SiC_2 specimens were buried in the powders and packed into an Al_2O_3 jar, which was then placed in a horizontal tube furnace under a flowing argon atmosphere. The heating rate for all runs was 10 °C/min. After treatment, the samples were cooled to room temperature in the furnace. In order to obtain an optimal boronizing condition, heat treatments were carried out at temperatures of 1100–1400 °C for 2–10 h. To determine growth kinetics of boronizing coatings, three runs were repeated in each treatment condition.

2.2. Characterization of boronizing coatings

After the boronizing treatments, the surface morphology and microstructure of coatings were investigated using an S-360 scanning electron microscope (Cambridge Instrument Ltd., UK) equipped with an energy dispersive spectroscope (EDS) system and a Tecnai-G2-20 transmission electron microscope (Philips, NE). Chemical compositions of the boronizing coatings were identified utilizing X-ray diffraction (Rigaku D/max-2500PC, Japan) and X-ray photoelectron spectroscopy (ESCALAB250, VG) using Al Kα (1486.6 eV) X-ray source with a power of 150 W. Survey and individual high-resolution spectra were recorded with a pass energy of 50 eV. And the detector work function was calibrated using the C1s peak at 284.5 eV of a highly oriented pyrolytic graphite (HOPG) sample. The background was subtracted by the method of Shirley, and the peaks were deconvoluted by the fitting of Gaussian–Lorentzian line shapes. The surface hardness of the boronized Ti_3SiC_2 ceramic was measured using a microhardness tester at an applied load of 100 N with a dwelling time of 15 s. The wear resistance was determined by a ball-on-disc method using a micro-mechanical property test system (CETR UMT-2, USA). All wear tests were performed in atmosphere environment (temperature, 25 ± 1 °C; relation humidity, 50 ± 5%) without a lubricant by pressing a GCr15 steel ball (ϕ 4.76 mm) on a rotating plate, made of modified or unmodified Ti_3SiC_2. A constant load of 10 N was applied, and the relative sliding speed was 40 m/min. Friction coefficients were recorded by a real-time mode and wear rates were determined by precisely measuring the weight change using a balance with a accuracy of 10^{-5} g.

3. Results

3.1. Microstructure and phase composition of boronizing coatings

After the boronizing treatments, the surface of Ti_3SiC_2 specimens turned into gray from original silvery white. X-ray diffraction analyses were performed on the specimens boronized at 1100–1400 °C for 8 h, the results are presented in Fig. 1. For comparison, the XRD pattern of untreated Ti_3SiC_2 is also plotted in Fig. 1. It is seen that all of the boronizing coatings are composed of TiB_2 and β-SiC. And the intensity of diffraction peaks of TiB_2 increases with increasing temperature, which suggests that increasing treatment temperature is in favor of the growth of the coatings. When the boronizing temperature is above 1300 °C, the coatings become thick so that those peaks corresponding to the Ti_3SiC_2 substrate disappear. In order to detect if there are any amorphous phases to form in the boronizing coatings, the coating treated at 1300 °C for 8 h was

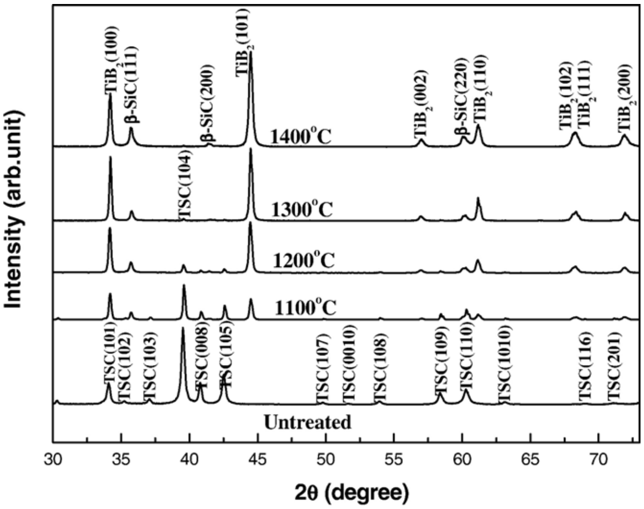

Fig. 1. XRD patterns of Ti_3SiC_2 before and after boronizing treatment at 1100–1400 °C for 8 h.