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Effect of reactive gas composition on the microstructure, growth mechanism and friction coefficient of TiC overlayers

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ABSTRACT

Titanium carbide overlayers were synthesized by gas phase carburization of titanium at 1150 °C with varying reactive gas compositions and durations. These layers were investigated by X-ray diffraction, tribometry, Raman spectroscopy and scanning electron microscopy. Titanium carbide layers exhibited very low coefficient of friction due to the presence of amorphous carbon on the surface. The growth mechanism and the surface microstructure of the layers showed a critical dependence on methane content in the reactive gas mixture.

1. Introduction

Titanium carbide is a material of great commercial importance due to its superior hardness, high melting point, excellent thermal and chemical stability. However, tribological properties like friction coefficient and wear resistance of TiC need to be improved [1]. Toward this end, attempts have been made to synthesize TiC with the addition of amorphous carbon, which acts as a solid lubricant [2,3,4]. Amorphous carbon residing at the surface greatly influences the surface mechanical properties of TiC [5]. Magnetron sputtering is an important technique to coat TiC and amorphous carbon [5,6,7]. Pulsed ion beam assisted carburization and plasma immersed ion implantation are also used for this purpose [8, 9]. We have synthesized titanium carbide overlayers by high temperature exposure of pure titanium metal to different concentrations of methane and for different exposure durations. The microstructural and mechanical properties of the formed layers showed a large dependence on methane content and exposure time.

2. Experimental

Metallographically polished and ultrasonically cleaned titanium specimens (12 × 12 × 2 mm) were suspended in a thermogravimetric (TG) analyzer (SETSYS 16/18, Setaram, France) cum exposure facility. Prior to sample heating, the system was evacuated and purged several times with high pure argon to minimize oxygen content and thereby avoid surface oxidation. High pure methane was used as the process gas. A heating rate of 10 °C/min and a process temperature of 1150 °C were maintained for all the experiments. The in-situ weight gain of the specimens was measured in the TG microbalance. As a general safety measure to protect the TG microbalance, methane was mixed with a constant amount of argon. Methane content and processing time were varied to optimize the conditions for synthesis of phase pure TiC with an objective to achieve minimum wear rate and lowest friction coefficient. Further experimental details can be found elsewhere [10]. Phase identification of coatings was carried out by X-ray diffraction (XRD) analysis in powder mode with Bragg-Brentano geometry using Cu-K_α radiation (STOE, X-ray powder diffractometer). Linear reciprocating mode of a ball on disk tribometer (CSM, Switzerland) was used to carry out tribological tests of the coatings. A spherical steel ball (100Cr6 SS) of Ø 6 mm with surface roughness 0.06 μm was used as a sliding body to measure the value of coefficient of friction, where normal load and sliding speed were kept constant at 5 N and 2 cm/s, respectively. Tests were performed at ambient (dry and unlubricated) conditions with a relative humidity of 62%. A Field Emission Scanning Electron Microscope (FESEM, Supra 55, Carl Zeiss, Germany) was used to observe the variation in microstructure and morphology of surface and wear tracks of the samples. Energy dispersive X-ray (EDS) analysis (INCA, Oxford Instruments, UK) attached to the FESEM equipment was used to explore the composition of the layers. Raman spectra were recorded using a micro Raman spectrometer (Invia, Renishaw, UK) on the virgin surface and wear tracks of the coatings using 532 nm wavelength from an argon ion laser at laser power of 5 mW. Surface roughness of the specimens was measured using an Atomic Force Microscope (Solver, NT-MDT, Russia).

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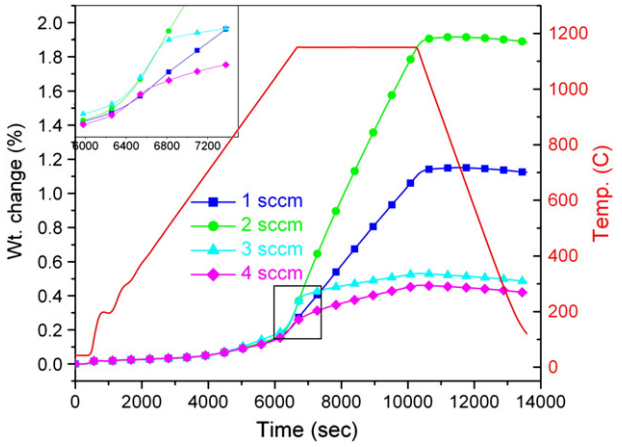

Fig. 1. TGA weight gain and temperature profiles are plotted against time for samples treated for 1 h with varying methane content. Inset is the initial part of the weight gain.

3. Results

3.1. TG analysis

The percentage weight gain and temperature profile of the specimens prepared for 1 h duration with different methane flow rates (1, 2, 3 and 4 standard cubic cm/min, sccm) are presented in Fig. 1. A quick perusal of the results clearly indicates that the total weight gain of the specimens does not linearly increase with methane content as one would have generally expected. For example, the sample treated at 2 sccm methane shows a maximum weight gain of 1.9% while the one treated at a higher flow of 4 sccm showed the minimum gain of 0.45%. The samples treated for 4 h also showed a similar trend. Here the sample processed at 2 sccm CH_4 showed the maximum gain of 4.8% and the minimum (1.4%) for the sample treated at 4 sccm. These observations suggest that the initial period of the reaction plays a crucial role in deciding further growth of the layers. Hence, the initial part of the weight gain is explored further and an expanded view is shown in the inset of Fig. 1 for better clarity. The results clearly indicate a difference in the trend of weight gain for the samples treated in various gas mixtures. The samples processed at higher methane content show a fast initial growth and a sharp change of slope during the isothermal region, whereas the samples with lower flow rate showed the trend of a diffusion controlled reaction. With higher flow rate, it seems, that the layer formed during the initial part of the reaction acts as a diffusion barrier and slows down further growth which eventually results in the formation of a thinner layer.

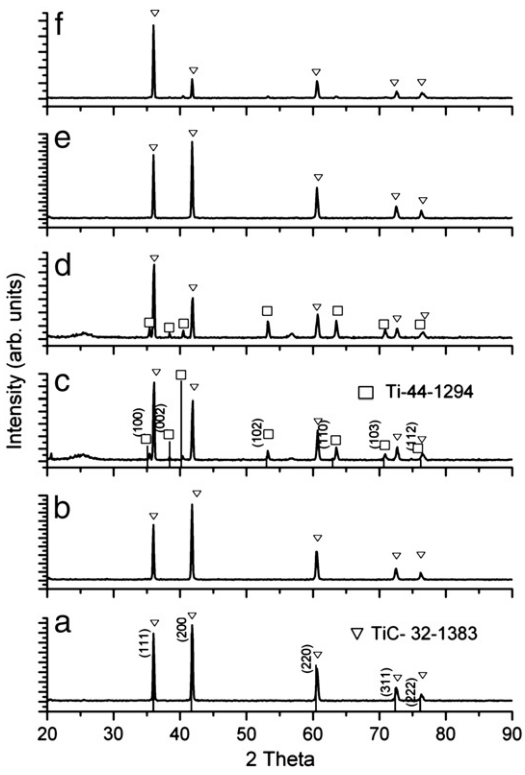

Fig. 2. Powder XRD patterns of samples treated in different methane flow and exposure times (a) 1 sccm, 1 h, (b) 2 sccm, 1 h, (c) 3 sccm, 1 h, (d) 4 sccm, 1 h, (e) 1 sccm 4 h and (f) 4 sccm, 4 h.

3.2. XRD measurements

The XRD patterns of the samples treated under different methane flow rates and durations are shown in Fig. 2(a–f). At lower flow rates (Fig. 2a and b, 1 sccm and 2 sccm), the layer formed is phase pure TiC (JCPDS no. 32-1383). It matches with the standard TiC with respect to number of peaks and their relative intensities. It does not show any additional peaks which indicate phase purity of TiC layer. Specimens treated in 3 sccm and 4 sccm CH_4 flow (Fig. 2c and d) show a different pattern. In addition to the TiC peaks, there are peaks corresponding to metal Ti (JCPDS no. 44-1294). This is due to the fact that the thickness of the layer formed with higher flow rate is smaller compared to that of lower flow rates (as evident from TG weight gain) and the X-rays penetrate the entire TiC layer to reach titanium substrate. It is also

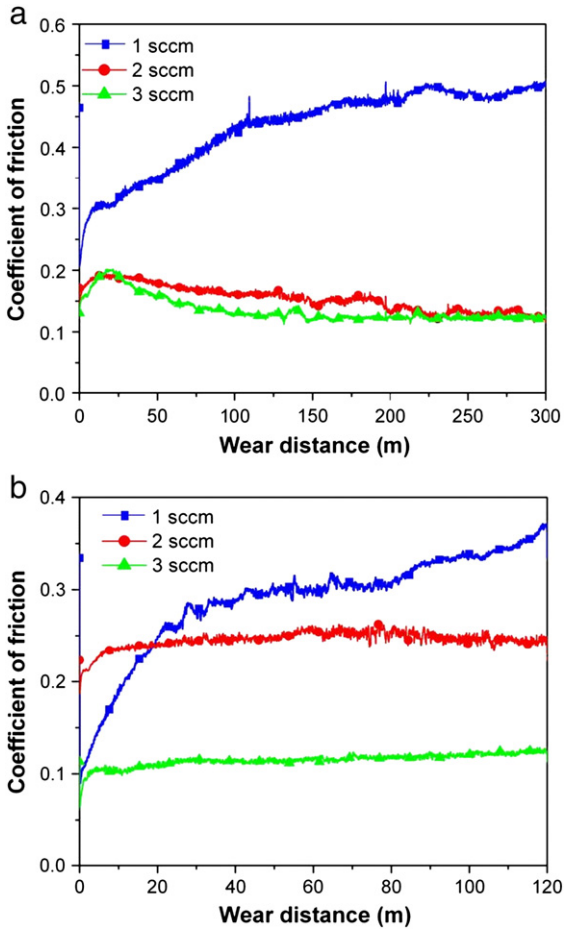

Fig. 3. Friction coefficients of samples treated for (a) 1 h and (b) 4 h durations plotted against wear distance.