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Oxidation behavior of TiC_xN_{1-x} coatings as a function of C/N ratio

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Abstract

Titanium nitride, carbide and carbonitride coatings were synthesized on titanium substrates by the thermochemical diffusion process in ammonia, methane and varying compositions of ammonia/methane mixture, respectively. High temperature oxidation resistance of these coatings has been studied as a function of carbon to nitrogen ratio in the coatings. Oxidation experiments were conducted in a thermogravimetric analyzer in oxygen atmosphere at 800 °C. XRD, SEM, EDS, XPS and Raman measurements before and after the oxidation studies revealed that the content of sp^3 bonded carbon interspersed in the coatings plays a key role in deciding the oxidation resistance of the coatings. TiC with higher sp^3 carbon showed maximum oxidation resistance and TiN the least. Incorporation of even a small amount of N in TiC and C in TiN is found to drastically alter their oxidation resistance.

Keywords: Oxidation; Raman analysis; Scanning electron microscopy; Thermogravimetry; Titanium carbonitride

1. Introduction

Titanium carbonitride (TiCN) has been widely accepted as a hard coating material and is also being used for the preparation of cermet (Ceramic–metal material) owing to its extraordinary mechanical and physical properties like high hardness, high melting point, and wear and corrosion resistance [1–3]. TiCN is basically a complex solid solution of TiN and TiC. Both TiN and TiC are isostructural (fcc) and totally miscible and hence the combination of the two in appropriate ratios (TiC_xN_{1-x}) can result in properties incorporating the advantages of both TiC and TiN [4–6]. Better wear properties of TiCN compared to TiN are attributed to its higher hardness and the carbon present in it acts as a lubricant leading to reduced friction and wear [7]. Compared to pure TiC coatings, TiCN coatings show better adhesion with the substrate due to its negligible internal stress [8,9]. Though a lot of literature is available on the oxidation behavior of TiN and TiC [10–13], not many studies have been carried out in the case of TiCN as a function of C/N ratio, particularly in the form of coatings. The available literature on TiCN is based on powder samples, comprising mixtures of TiN and TiC in different ratios [14] or on TiCN based cermets [15,16]. Hence, a study has been taken up to ascertain the oxidation behavior of TiC_xN_{1-x} coatings as a function of C/N ratio at 800 °C, which is well above the recommended operating temperature window for both TiN and TiC.

2. Experimental details

Titanium carbonitride (TiC_xN_{1-x}) coatings were synthesized with varying C/N ratios by gas phase carbonitridation of Ti for 4 h in methane–ammonia gas mixture at 1050 °C. The synthesis and characterization of TiC_xN_{1-x} are discussed in our earlier publication [17]. The composition of the process gas mixtures was varied to achieve the coatings with different concentrations of C and N. The NH_3, CH_4 gas mixtures used were of composition 100:0, 80:20, 65:35, 50:50, 35:65, 20:80 and 0:100. The samples grown in these atmospheres are identified as C-0, C-20, C-35, C-50, C-65, C-80 and C-100, respectively, where C represents CH_4 and the number indicates its percentage. The total flow of the two reactive gases was maintained at 4 sccm. Being a non-line of the sight process, the coatings prepared by thermochemical diffusion cover the entire

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surface of the specimen uniformly. This is an essential requirement for oxidation studies to minimize the errors arising out of exposure of uncoated surface/substrate. In the present study, these specimens were subjected to oxidation at 800 °C in O_2 (20%)+ Ar gas mixture for 5 h each in a thermogravimetric analyzer (TGA). Weight change of the specimens was continuously recorded. Initial heating rate of the TGA furnace was maintained at 15 °C/min. Phase identification of coatings before and after the oxidation was carried out by X-ray diffraction (XRD) analysis in powder mode with Bragg–Brentano geometry using Cu Kα radiation (STOE, X-ray powder diffractometer). A Field Emission Scanning Electron Microscope (FESEM, Supra 55, Zeiss, Germany) was used to examine the variation in microstructure and morphology of surface of the samples. Energy dispersive X-ray (EDS) analysis (Oxford Instruments, UK) attached to the FESEM equipment was used to explore the composition of the layers. Raman spectra of the virgin and oxidized samples were recorded using a micro-Raman spectrometer (Invia, Renishaw, UK) with 5 mW/514 nm argon ion laser. X-ray photoelectron spectroscopy (XPS, SPECS, 150 mm detector, Germany) of virgin samples was carried out using Al Kα radiation.

3. Results and discussion

3.1. Oxidation of TiCN specimens

Oxidation of the specimens was carried out in the thermogravimetric analyzer in oxygen/argon atmosphere. Prior to oxidation, the analyzer chamber was evacuated and filled with O_2+Ar gas mixture repeatedly to maintain reproducibility of the experiments. Samples were hung from the microbalance of the TGA by a Pt wire hook, such that all the surfaces of the specimens were exposed to the active gas. Oxygen concentration in the atmosphere was maintained at 20%. Experiments were carried out for 5 h each at 800 °C while the temperature and the weight change of the specimens were recorded continuously. Subsequently the TGA system was allowed to cool naturally to room temperature in argon atmosphere.

3.2. TGA results

TGA weight gain profiles during oxidation of all the samples are shown in Fig. 1. The actual weight gain is converted to weight gain per surface area for better comparison. The minimum and maximum weight gains were experienced by TiC (C-100) and TiN (C-0), respectively. The difference in weight change due to conversion of TiC to TiO_2 and TiN to TiO_2, being negligible, is not accounted in the estimates. From the plots it is clear that TiC is the most oxidation resistant of all the specimens and TiN the least in the present environment. However, the noteworthy findings from weight gain results are that a small addition of carbon to TiN layer (sample C-20) improves its oxidation resistance drastically, while an addition of small amount of nitrogen (sample C-80) reduces the oxidation resistance of TiC substantially. This trend is seen for other samples also (Fig. 1: C-35, C-65).

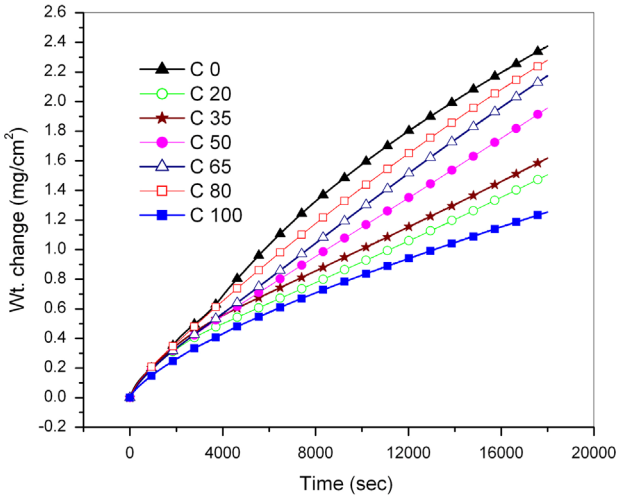

Fig. 1. Weight gain profile of various specimens treated at 800 °C for 5 h in oxygen–argon gas mixture.

Table 1
Inception temperature and weight gain for different specimens during oxidation studies.

Methane concentration (%)	Inception temperature (°C)	Wt. gain (mg/cm^2)
100	733	1.25
80	699	2.28
65	700	2.17
50	717	1.95
35	715	1.61
20	724	1.50
0	711	2.37

When the carbon to nitrogen ratio approaches unity (C-50), the specimen is found to have an average oxidation resistance. In order to understand the drastic effect of small addition of C or N on oxidation, the initial weight gain during ramp segment was carefully analyzed. From the weight change during the initial ramp (not shown), it was noticed that the effective weight gain is initiated at different temperatures for various samples and these temperatures are shown in Table 1. The inception temperature for the oxidation of TiC (100% CH_4) was 733 °C. Addition of a small amount of ammonia in to the system (20%) reduces the inception temperature to 699 °C. This has also reflected as enhanced weight gain compared to TiC in isothermal heating (Fig. 1 and Table 1). The inception temperature for the oxidation of TiN (C-0) is increased from 711 °C to 724 °C with the addition of 20% methane (C-20) and resulted in improved oxidation resistance. Similar trend is observed for all the specimens. From this it is clear that the oxidation resistance and the inception temperature are critically dependent on the carbon/nitrogen concentration in the coatings.

3.3. XRD results

Fig. 2(a) and (b) shows the XRD results for C-0, C-20, C-50, C-80 and C-100 before and after the oxidation