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ScienceDirect
Surface & Coatings Technology 201 (2006) 2818–2821
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Effect of preheating temperature on the deposition rate of TiCN

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Received 23 November 2005; accepted in revised form 23 May 2006
Available online 17 July 2006

Abstract

The vaporizing process of the liquid precursors $TiCl_4$ and CH_3CN for the TiCN deposition was investigated theoretically and experimentally. Dependence of the TiCN deposition rate on preheating temperature of $TiCl_4$ and CH_3CN was observed. It was found that the TiCN deposition rate with the preheating temperature of 110 °C is less than half of the deposition rate at 50 °C. Through thermodynamic calculations, it was discovered that the $TiCl_4$ and CH_3CN vapor phases were not fully generated if the preheating temperature is too low. If the preheating temperature is too high, gas phase reactions may cause loss of Ti resulting in lower TiCN deposition rates.

Keywords: TiCN; Preheating; CVD

1. Introduction

Advanced cemented carbide inserts are typically coated with multi-layers including titanium carbonitride (TiCN), alumina (Al_2O_3), and titanium nitride (TiN). In a previous work, we studied the deposition conditions for an interlayer between TiCN and Al_2O_3 for forming α-Al_2O_3 [1,2]. In the present work, we focus on the deposition conditions for TiCN coating.

The development of commercial TiCN coatings in the past few years has been stimulated by an increase in flank wear resistance (resistance to abrasion) when compared to titanium nitride (TiN) coatings due to the higher hardness of TiCN [3, 4]. Karlsson et al. [5] showed that for arc evaporated $TiC_{1-x}N_x$, there was an increase in hardness with x to a maximum at $x=0.4$–0.7 in coatings produced in laboratory.

Since CH_3CN (acetonitrile) provides CN radicals to maintain the C/N ratio, it is used in the present work to provide the C and N sources. $TiCl_4$ (titanium tetrachloride) was used as the Ti precursor. Both are high purity grades. As both chemicals are liquid at room temperature, a vaporizer is used to generate the mixture of these two precursors. Furthermore, the two precursors are preheated before entering the vaporizer. In the present work, the effect of preheating temperature on the deposition rate of TiCN coatings was investigated experimentally and computationally along with the discussion of the vaporizer temperature.

2. Experiments and calculation procedures

The TiCN depositions were conducted at Kennametal Inc. in a lab-scale CVD chamber with the rising gas flow pattern and H_2 as the carrier gas. $TiCl_4$ and CH_3CN were stocked in cylinders at the liquid state, vaporized and mixed evenly in a vaporizer before being fed into the CVD chamber. To help vapor generation, a heat-block was used to preheat the two liquids. A schematic picture of the heat-block and vaporizer is shown in Fig. 1. At the bottom of the vaporizer, Al_2O_3 beads were stocked to provide preheating for the H_2 carrier gas. The temperature of the vaporizer was kept constant at 130 °C, measured by thermocouples at two different locations. A pressure gauge was placed above the vaporizer to measure the pressure ranged from 76 to 100 Torr. Two preheating temperatures of the heat-block, 50 and 110 °C, were tested. A mixture of $TiCl_4$ (2.7%), CH_3CN (0.9%) and H_2 (96.4%) was used for the deposition where the compositions were calculated

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doi:10.1016/j.surfcoat.2006.05.034

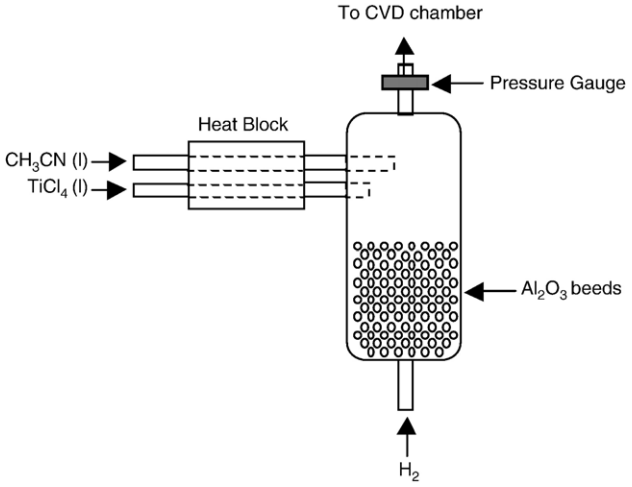

Fig. 1. Schematic drawing of the vaporizing system.

by converting liquid $TiCl_4$ and CH_3CN to ideal gas at 25 °C and 1 atm. After depositions, samples were taken out from the CVD chamber and examined by means of optical microscopy and X-ray diffraction (XRD) techniques (PANalytical Xpert MPD with Bragg focusing optics and Copper long fine focus tube at 45 kV and 40 mA).

Thermodynamic calculations were carried out using the Thermo-Calc program [6] and the SGTE substance database [7] with the Gibbs energy functions of liquid CH_3CN and TiCN from Ref. [8] and TiCN from FEDAT [6]. The effects of individual processing parameters, i.e. composition, temperature, and pressure and their combinations on the phase stability were investigated by systematically varying their values to explore possible reactions during vaporization.

3. Results and discussions

The vapor pressures of $TiCl_4$ and CH_3CN were calculated and shown in Fig. 2 with three regions marked as A, B, and C. In region C, both of $TiCl_4$ and CH_3CN are in the liquid state. In region B, $TiCl_4$ remains liquid and CH_3CN becomes gas. In region A, both chemicals are in the gas state. Table 1 shows the preheating temperature ranges for the three regions at 76 Torr and 100 Torr, respectively. For both $TiCl_4$ and CH_3CN to be efficiently carried into the CVD chamber, it is intuitive to think that both should be in the gas state when they pass through the heat block, i.e. the preheating temperature should be higher than 37 °C at 76 Torr and 42 °C at 100 Torr.

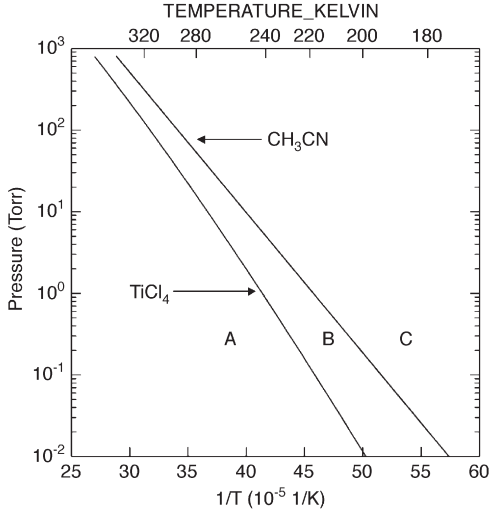

Fig. 2. Vapor pressure curves for $TiCl_4$ and CH_3CN.

Table 1
Preheating temperature ranges for the three regions in Fig. 2

Pressure	Region A	Region B	Region C
76 Torr	$T>37$ °C	37 °C$>T>$14 °C	$T<14$ °C
100 Torr	$T>42$ °C	42 °C$>T>$20 °C	$T<20$ °C

The results of two tests of the TiCN deposition were shown with the preheating temperatures to be 50 and 110 °C in Fig. 3. The X coordinate is the location of the samples in the center of the loading zone of the CVD chamber from the bottom to the top with the distance between two neighboring locations being 3.8 cm. The Y coordinate is the TiCN thickness of the samples. It is clear to see that the thicknesses of the TiCN layer at 110 °C is about half of the thicknesses at 50 °C. It has also been noted that the TiCN layer is thin without preheating.

After the TiCN depositions, some residues were found at the bottom of the vaporizer. An XRD spectrum of the residues is shown in Fig. 4 with poor signals, which may be partly due to the extremely fine grain size of residual powders. The residue appears to consist of chlorides with the strong peak around 33° possibly corresponding to $(11\bar{3})$ of $TiCl_3$. This suggests a chemical reaction in the vaporizer, which may reduce the amount of precursors brought into the CVD chamber, and thus reduces the TiCN deposition rate.

Hence, the effects of the processing parameters, i.e. preheating temperature, pressure and gas flow ratios, were investigated thermodynamically. Fig. 5 shows the effect of temperature and pressure while the composition is fixed. Due to the gas phase existing in all the phase regions, the phase regions are labeled only with solid phases. It is observed that if a complete equilibrium is reached in the system at temperatures below the boundary of the $TiCl_3$ and $TiCl_3+NH_4Cl$ phase

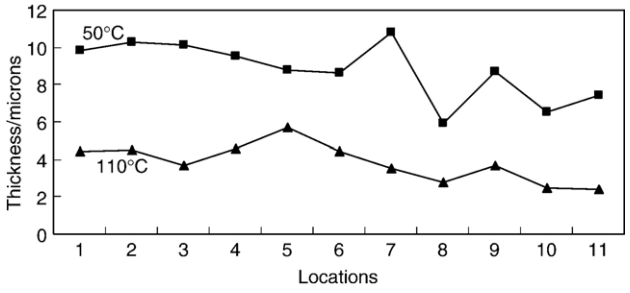

Fig. 3. The thickness of the TiCN layer vs. location with the distance between two neighboring locations being 3.8 cm and sample location in the center of the loading zone.