



Chemical vapor deposition of TiN on transition metal substrates

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ABSTRACT

The growth of chemical vapor deposited TiN from a reaction gas mixture of TiCl_4 , N_2 and H_2 was investigated on three different transition metal substrates: Fe, Co and Ni at deposition temperatures ranging from 850 °C to 950 °C. The interactions between the substrate metals and the gas phase were investigated using thermodynamic calculations. The TiN coatings were characterized by scanning electron microscopy, scanning transmission electron microscopy, X-ray diffraction, energy dispersive X-ray spectroscopy and transmission Kikuchi diffraction.

Chemical vapor deposition (CVD) of TiN on Co substrates resulted in dense, columnar coatings of single phase TiN. The activation energy for TiN deposition on Co was determined to be 90 kJ/mol. CVD of TiN on Fe substrates caused severe substrate corrosion by the formation of gaseous FeCl_x . Due to the substrate corrosion, the activation energy could not be determined. Furthermore, it was found that CVD of TiN on Ni substrates produced a phase mixture of TiN and Ni_3Ti . Formation of Ni_3Ti could be minimized by decreasing the H_2 partial pressure and increasing the N_2 partial pressure. Deposition on Ni yielded two different activation energies, 40 kJ/mol in the temperature interval 850 °C to 900 °C and 165 kJ/mol in the interval 900 °C to 950 °C. This is an indication of two different types of process control, which were identified as Ni diffusion into the growing film and a gas phase processes. The results of the present study showed that CVD of TiN on a cemented carbide using Fe and Ni in the binder phase, must be optimized in order to avoid corrosion or unwanted phases. Methods to achieve this are presented in this paper.

1. Introduction

Cemented carbide (WC with Co as a binder phase) based cutting tools have, for decades, been the primary choice in the metal forming industry. Lately, concerns regarding the toxicity of cobalt powder have increased, thereby driving the development for alternative binder phase materials [1,2]. Fe and Ni have been evaluated as such an alternative, showing promising results [3]. At the same time, the demands for higher quality and productivity are steadily increasing and the need to develop high performance tools is greater than ever. To increase the wear resistance of a cutting tool, hard protective coatings are typically applied by either chemical vapor deposition (CVD) or physical vapor deposition (PVD), depending on the intended use of the tool. CVD coated WC-Co cutting tools are often coated with a multilayer system comprising $\text{TiN-Ti(C,N)-Al}_2\text{O}_3$, where TiN is the layer closest to the tool material. A general prerequisite for CVD is that the substrate needs to be relatively inert towards the reaction gas-mixture in order to prevent substrate degradation (often by corrosion). If the binder phase of the

WC-Co is changed, the interactions between the gas phase and the new binder needs to be investigated in order to maintain a high performance of the coating/substrate.

CVD of TiN on cemented carbides (WC/Co) is a well-known process [4–9]. Investigations of TiN deposition onto several binder phase candidates such as Ni and stainless steel have been performed, where a different growth rate, texture and coating morphology was observed on CVD of TiN [10,11]. The adhesion of the TiN coating was also lowered. As shown in previous studies the diffusion of binder phase material into the coating can also have a substantial impact on the coating adhesion [8,12,13]. In a study of CVD coating adhesion on WC substrates using different binder phases (Fe, Ni and Co based) it was found that Co containing substrates had the best tool-coating adhesion [3].

Porous coatings generally have poor mechanical properties, such as hardness and adhesion, and are thus not ideal for metal cutting applications. CVD growth of TiN on Ni surfaces have shown that the coating becomes porous and consists of more than one phase [11,13,14]. The cause of this behavior is suspected to arise from the interaction between

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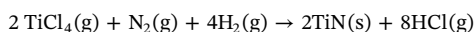
TiCl₄ and Ni to form Ni-chlorides in the gas phase. These compounds are reduced and redeposited on the TiN surface to form the inter-metallic compound Ni₃Ti. The reported growth of TiN on Ni substrates suggests that the required mechanical properties for cutting tool use cannot be achieved. However, through a better understanding of the interface chemistry during CVD of TiN the formation of inter-metallic phases can be suppressed.

The suggested rate limiting step in CVD of TiN from the TiCl₄-N₂-H₂ system in conditions where mass transport influence is minimal, is breakage of H–H and N≡N bonds on the growing surface [15]. The required dissociation and recombination energies for both gases depends on the surface. Of importance for the surface reactions are the surface chemical composition, the surface structure and therefore the crystallographic orientation of the surface [16]. Another important reaction involved in the formation of TiN from the TiCl₄-N₂-H₂ reaction gas mixture is the homogeneous reduction of TiCl₄ to TiCl₃ and TiCl₂ in the gas phase where TiCl₃ is believed to be the main Ti growth species. The reduction reaction TiCl₄ → TiCl_{4-x} is favored in the presence of hydrogen through the formation of HCl instead of Cl₂ [17–19]. Furthermore, it was shown in [19] that TiCl_{4-x} does not form in significant amounts in the absence of H₂ at temperatures ≤ 1000 °C. In the presence of H₂ the onset of TiCl_{4-x} formation occurs at significantly lower temperatures, ~800 °C [19]. TiN is normally deposited in an excess of H₂, thus enabling fast reduction of TiCl₄ to TiCl_{4-x}. However, CVD in a H₂ deficient atmosphere may shift the TiCl₄/TiCl₃ equilibrium and reduce the reactivity of the Ti-precursor.

In this paper the growth mechanism of CVD of TiN on binder phase candidates Fe and Ni have been investigated. The insights in the growth mechanism will be used to propose a deposition method for TiN coatings suitable for cutting tool applications where Fe and/or Ni is used as binder. Thermodynamic calculations were performed to predict and interpret the experimental results. Co substrates were used as a reference in all experiments. Pure metallic substrates were implemented in this study, in order to clarify the effect of changing the binder, as in most previous cases alloys were studied and thus the effect of each metal is unclear.

2. Material and methods

An Ionbond 530 hot wall CVD reactor was used to deposit TiN layers on Co, Fe and Ni substrates. The overall chemical reaction for the TiN formation can be described as:



The deposition conditions are shown in Table 1. Five depositions were made with a step wise (25 °C) increase of temperature between 850 and 950 °C. One deposition was performed at 950 °C with a reduced H₂ partial pressure compared to the other depositions. The

Table 1
Temperature, partial pressures for all gases and deposition time for the TiN depositions.

T (°C)	H ₂ (kPa)	N ₂ (kPa)	TiCl ₄ (kPa)	P _{tot} (kPa)	Deposition time (h)
850	42.2	16.7	1.1	60	7.5
875	42.2	16.7	1.1	60	5.0
900	42.2	16.7	1.1	60	4.5
925	42.2	16.7	1.1	60	4.5
950	42.2	16.7	1.1	60	2.3
950 (reduced H ₂)	7.6	51.3	1.1	60	2.3

deposition time was adjusted to give the same film thickness for all depositions.

The Fe substrates were produced by pressing and arc melting Fe powder (Alfa Aesar, 99.9%). The Fe substrates were ground flat using SiC paper and polished to a mirror finish using 6, 3 and 1 μm diamond suspensions as final polish. Polished metallic Co (99.5% and Ni(99.9%) substrates (10 × 10 × 1 mm) were supplied by MTI Corp.

The phase content of the TiN coatings were analyzed using grazing incidence X-ray diffraction (GI-XRD) at 1° incidence angle, using a Philips MRD-XPRT diffractometer. An incident beam X-ray mirror was used in all measurements. For the coatings deposited on Ni substrates, a 0.27° parallel plate collimator and a 0.04 rad Soller slit were used on the diffracted side. For the coatings deposited on Fe and Co substrates a 0.18° parallel plate collimator, flat graphite monochromator and 0.04 rad Soller slit were used on the diffracted side.

Polished cross sections of the deposited coatings were produced by cutting with an alumina high-speed cutter and casting into Bakelite. The cast samples were ground flat using SiC paper (120 – 1000) and then polished using a diamond slurry (6, 3 and 1 μm particle sizes) followed by a final polish using colloidal SiO₂.

A lamella from one of the Ni samples (deposition temperature 950 °C) for investigations by scanning transmission electron microscopy (STEM) and transmission Kikuchi diffraction (TKD) was produced using the Focused ion beam (FIB) in-situ lift out technique by an FEI Strata DB 235 instrument [20]. Film morphology, cross section thicknesses, elemental composition and local phase composition of the CVD coatings were measured using a Zeiss Merlin High-resolution scanning electron microscope (HR-SEM). Coating growth rates were calculated by dividing cross section thickness with deposition time. Elemental composition was measured using energy dispersive x-ray spectroscopy (EDS) with an X-Max 80 mm² silicon drift detector. Local phase composition was measured by TKD measurements using an Oxford Nordlys EBSD detector.

A probe corrected Titan Themis operating at 200 keV was used for the TEM measurements. STEM images were acquired using a high angle annular dark field detector (HAADF). STEM-EDS analysis was performed using a SuperX – EDS detector.

3. Thermodynamic calculations

To aid the interpretation of the experimental results thermodynamic calculations were performed. The same experimental parameters as in the depositions were applied. One set of calculations was made for each of the substrate metals, the substrate metal was kept in a large excess to reflect the experimental conditions. To get the highest possible accuracy of the calculations all possible condensed and gaseous reaction products were included. 43 reaction products for CVD on Co substrates, 44 reaction products for CVD on Ni substrates and 51 reaction products for CVD on Fe substrates were included. For a detailed list of all species, see Appendix A, Table A1. A free-energy minimization technique was used, (program Ekvicalc [21]) This method was implemented to predict the behavior of CVD processes in several studies, thereby confirming the validity of the method [15,22,23]

4. Results and discussion

4.1. Thermodynamic calculations

The yield of substrate chlorides in the gas phase as a function of

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