

# Development of moderate temperature CVD $\text{Al}_2\text{O}_3$ coatings

R. Connelly <sup>a</sup>, A.K. Pattanaik <sup>b</sup>, V.K. Sarin <sup>a,\*</sup>

<sup>a</sup> Department of Manufacturing Engineering, College of Engineering, Boston University, 15 St. Mary's Street, Brookline, MA 02246, USA

<sup>b</sup> Sandvik Coromant, 1702 Nevins Road, Fair Lawn, NJ 07410, USA

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## Abstract

Chemically vapor deposited  $\text{Al}_2\text{O}_3$  coatings, due to their high hardness and chemical inertness, are currently the state of art in the cutting tool industry. The conventional high deposition temperature of about 1050 °C for  $\text{Al}_2\text{O}_3$  coatings, based on the water–gas shift process, has to a great extent restricted the development of several hybrid coatings, such as TiC/TiN/TiCN/ $\text{Al}_2\text{O}_3$ . To overcome this limitation, alternate systems to deposit  $\text{Al}_2\text{O}_3$  at moderate temperatures have been investigated. Systems using  $\text{NO}-\text{H}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NO}_2-\text{H}_2$  and  $\text{HCOOH}$  were identified and thermodynamic calculations were performed to evaluate them as potential sources of oxygen donors to form  $\text{Al}_2\text{O}_3$  in the moderate temperature range of 700–950 °C. Preliminary results have clearly demonstrated that it is possible to grow moderate temperature alumina (using such alternate sources) on the TiC/TiN coated cemented carbide substrates.

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**Keywords:** Chemical vapor deposition (CVD);  $\text{Al}_2\text{O}_3$ ; Medium temperature; Thermodynamics; Cutting tools

## 1. Introduction

Chemical vapor deposition of  $\text{Al}_2\text{O}_3$  coatings are commonly used in the cutting tool industry because of their hardness, wear resistance, electrical insulating properties and chemical inertness especially in oxidizing environments [1]. Compatibility problems between the substrate (cemented carbide) and  $\text{Al}_2\text{O}_3$  typically require the use of an intermediate layer (such as TiC, Ti(C,N), TiN) in order to enhance adhesion and thermal shock resistance, with added benefits of improved wear, and toughness. Commercially CVD  $\text{Al}_2\text{O}_3$  is generally deposited using the water–gas shift reaction at temperatures around 1050 °C, while TiC and TiN can be efficiently deposited in the 700–900 °C range, making the one-step deposition cycle highly inefficient and expen-

sive. Although such coatings have been commercially available for more than two decades, attempts to modify this process have so far not been successful. The major hurdle stems from trying to reduce the deposition temperature of the  $\text{Al}_2\text{O}_3$ , since it takes a specific amount and rate of water–gas to form crystalline  $\text{Al}_2\text{O}_3$  and a given specific.

Extensive work has been reported on attempts to try and reduce the deposition temperature of CVD  $\text{Al}_2\text{O}_3$  coatings on pre-coated cemented carbide cutting tools [1–11]. Several investigations have been focused on creating water–gas using sources other than the conventional  $\text{H}_2-\text{CO}_2$  system (Table 1). Although many of these have reported limited success, to this point none have been viable for reasons including gas phase nucleation and non-uniformity in the coatings.

One of the compelling reasons for attempting to lower the temperature is that it would allow for a hybrid one-step TiC/TiN/TiCN– $\text{Al}_2\text{O}_3$  coating. A significant saving in cost would be realized as both the TiC/TiN

\* Corresponding author. Tel.: +1 617 353 6451; fax: +1 617 353 5548.  
E-mail addresses: [arun.pattanaik@sandvik.com](mailto:arun.pattanaik@sandvik.com) (A.K. Pattanaik), [sarin@bu.edu](mailto:sarin@bu.edu) (V.K. Sarin).

Table 1  
CVD Al<sub>2</sub>O<sub>3</sub> coatings using various oxygen donor systems

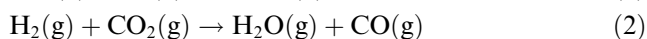
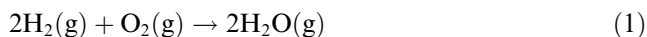
CVD system	Temperature (°C)	References
AlCl <sub>3</sub> /C <sub>2</sub> H <sub>5</sub> OH	700–1200	[12]
AlCl <sub>3</sub> /N <sub>2</sub> O/H <sub>2</sub>	997	[13]
AlCl <sub>3</sub> /NH <sub>3</sub> /CO <sub>2</sub>	770–900	[14]
AlCl <sub>3</sub> /O <sub>2</sub> /H <sub>2</sub> O	900–1400	[15]
AlCl <sub>3</sub> /O <sub>2</sub> /Ar	1050	[16]
AlX <sub>3</sub> /CO <sub>2</sub> /H <sub>2</sub> (X = Cl, Br, I)	1050–1500	[17]
AlBr <sub>3</sub> /NO/H <sub>2</sub> /N <sub>2</sub>	910	[18]
AlBr <sub>3</sub> /NO/H <sub>2</sub> N <sub>2</sub>	900	[19]

and Al<sub>2</sub>O<sub>3</sub> could be deposited within the same temperature range. Additionally lowering the Al<sub>2</sub>O<sub>3</sub> deposition temperature would also lower the inherent residual stresses in the coating that tend to cause cracking of the Al<sub>2</sub>O<sub>3</sub> coatings. Based on thermodynamics analysis, kinetic modeling was performed to establish alternate systems that could yield crystalline Al<sub>2</sub>O<sub>3</sub> coatings at moderate temperatures (between 700 and 950 °C). Some preliminary experimental were also conducted to test results from these models.

## 2. Thermodynamic analysis

Chemical thermodynamics of a CVD system under several different process parameters (reactant gas flow rate, temperature, and pressure) can help ascertain products that can form under equilibrium conditions. Because thermodynamics deals with equilibrium situations, and CVD is *not* an equilibrium process, it can not definitively determine what products will form. Rather, thermodynamics predicts what can possibly form and help develop a CVD process model as a starting point.

The concept driving the selection of an alternate water–gas source is to find a gas or gases that mimic the formation of water–gas from the H<sub>2</sub>–CO<sub>2</sub> reaction at lower temperatures. The molar quantity and rate of formation of water–gas in a reaction is an indirect indication of how much Al<sub>2</sub>O<sub>3</sub>, if any, can be deposited. It is well established that CVD Al<sub>2</sub>O<sub>3</sub> can only be deposited when a specific amount of water–gas is present in the system. Too much leads to gas-phase nucleation, or powdering, whereas insufficient amount can result in amorphous or no deposit at all. The water–gas shift reaction has been extensively investigated and recognized as the primary rate limiting steps for the growth of the crystalline Al<sub>2</sub>O<sub>3</sub> [20]. Water–gas can be generated in situ by reacting H<sub>2</sub> and oxygen donors like, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, etc. or by introducing H<sub>2</sub>O directly by means of a carrier gas.



According to Eq. (1), O<sub>2</sub> reacts with H<sub>2</sub> instantaneously above 400 °C and the gas mixtures with H<sub>2</sub>/O<sub>2</sub> = 2:1 are explosive [20]. The kinetics of the homogeneous gas phase reaction (2) have been studied in the temperature range between 400 and 1050 °C [21]. The rate of water formation in between 400 and 800 °C temperature range can be expressed as

$$d[\text{H}_2\text{O}]/dt = 7.6 \times 10^4 \cdot e^{-39200/RT} \cdot [\text{H}_2]^{1/3}[\text{CO}_2] \quad (3)$$

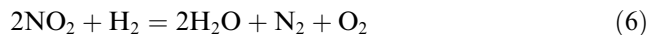
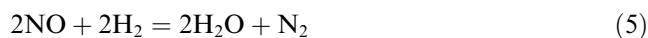
and in between 800 and 1050 °C as

$$d[\text{H}_2\text{O}]/dt = 1.2 \times 10^{13} \cdot e^{-78000/RT} \cdot [\text{H}_2]^{1/2}[\text{CO}_2] \quad (4)$$

According to the above equations, the water formation rate at a fixed temperature depends on the concentration of both H<sub>2</sub> and CO<sub>2</sub> and a maximum water formation rate is obtained at a CO<sub>2</sub>/H<sub>2</sub> molar ratio of 2/1. It has been experimentally confirmed that the AlCl<sub>3</sub>/H<sub>2</sub>O process is a fast reaction; AlCl<sub>3</sub>/O<sub>2</sub> is a very slow reaction, whereas aluminum oxide deposition from AlCl<sub>3</sub>/H<sub>2</sub>/CO<sub>2</sub> gas mixture used frequently [17,22,23], is a medium rate process [24] that yields the best crystalline deposits. High temperature kinetics studies of the chemical reactions of the CVD Al<sub>2</sub>O<sub>3</sub> coatings from AlCl<sub>3</sub>/H<sub>2</sub>/CO<sub>2</sub> gas mixture have been discussed elsewhere [25,26].

Using the program facility for the analysis of chemical thermodynamics (FACT), several thermodynamic calculations were performed on candidate systems to investigate the possibility of finding an alternate source of oxygen donors to form water–gas at lower temperatures. For each system the water–gas reaction was studied between 700 and 950 °C at a total pressure of 75 Torr. Both the molar quantity of water–gas formed and free energy formation of the reaction were examined.

Based on preliminary results the following systems were selected as possible oxygen donors to form water–gas at lower operating temperature for CVD alumina coatings.



Using the conventional process parameters for the AlCl<sub>3</sub>–H<sub>2</sub>–CO<sub>2</sub> in our CVD system, we empirically determined that at least 0.58 moles of water–gas was necessary to deposit an acceptable crystalline alumina coating. All of the selected systems, with the exception of formic acid with argon as a carrier gas, produce a water–gas amount of at least 0.6 moles (Fig. 1). However satisfying this criterion alone, as previously discussed, does not guarantee the formation of crystalline Al<sub>2</sub>O<sub>3</sub> deposits. Instead, the concentration and rate of formation of water–gas would have to mimic that of the conventional H<sub>2</sub>–CO<sub>2</sub> system, as closely as possible,

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