

Pyrolytic laser-based chemical vapour deposition of TiC coatings

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Abstract

TiC layers have been successfully deposited locally on D2 tool steel specimens and miniature industrial tools with the aim to improve their mechanical and chemical surface properties. The deposition process was based on a pyrolytically-induced chemical reaction of TiCl_4 and CCl_4 compounds combined with an atomic hydrogen source. Local heating of the substrate was achieved by means of a 100 W CO_2 laser controlled by a microcomputer-based feedback loop system, involving on-line substrate temperature monitoring. Scanning electron microscopy, energy-dispersive X-ray analysis, X-ray diffraction, and transmission electron microscopy analysis showed that close-stoichiometric TiC (fcc structure, lattice constant $a = 4.2 \text{ \AA}$) was deposited in the films with a nanocrystalline structure. The microhardness of the coatings was in the range 2500–3200 HK.

Keywords: Carbides; Chemical vapour deposition; Deposition process; Titanium carbide

1. Introduction

Refractory compounds of Ti (such as TiC, TiN and TiB_2) are often used as coatings in single-layer or multilayer form on steel substrates to enhance wear, corrosion and high-temperature oxidation resistance. Titanium carbide is a refractory material [1] which combines ceramic properties such as high melting point (3067 °C), high hardness (2800 HV), thermal and chemical stability, wear and corrosion resistance, and certain metallic properties such as low friction coefficient, high electrical and thermal conductivity. Consequently, it can be used as protective coating against thermal, chemical, and mechanical wear. Typical applications include high-performance cutting and forming tools, high corrosion resistance coatings for molten metal containers, thermal barrier in fusion and chemical reactors and diffusion barrier in semiconductor technology during the chemical vapour deposition (CVD) process.

Conventionally the formation of TiC [2,3] is based on the reaction between precursor compounds under appropriate temperature and pressure. $\text{TiCl}_4/\text{C}_2\text{H}_6/\text{H}_2$, $\text{TiCl}_4/\text{CCl}_4/\text{H}_2$ and $\text{TiCl}_4/\text{CH}_4$ are used as gas mixture at reaction temperatures in the range of 850 to 1250 °C. These temperatures can cause property changes and/or thermal damages in certain substrates. More specifically in tool steels, temperatures above 700–800 °C can cause overaging of carbides and dete-

rioration of hardness. Dimensional distortions are also likely to occur at the same temperature ranges. The need for a lower deposition temperature together with the need for local deposition led to the development of laser-based chemical vapour deposition (LCVD).

The LCVD techniques can be divided into two main categories depending on whether the laser beam interacts with the reactant gases or the substrate material. In photolytic LCVD the laser beam is absorbed by the reactant gases which undergo photodissociation, whereas in the pyrolytic process the substrate is heated locally by the laser beam and the chemical reaction is thermally induced.

LCVD of TiC on stainless steel has been demonstrated for the first time by Mazumder and Allen [4] where a $\text{TiCl}_4/\text{CH}_4$ reaction gas mixture and a 1.4 KW CO_2 laser were used. Allen [5] compared various combinations of substrate/coating material and concluded that TiC on stainless steel is quite difficult due to the steels high reflectivity at the 10.6 μm wavelength and high thermal conductivity. Umezada et al. [6] have also deposited TiC films on stainless steel by LCVD using a Nd:YAG laser. Other investigators deposited TiC on various substrate materials such as silica [7] and carbon fibers [8] using 200–400 W CO_2 lasers. Westberg et al. [9] have investigated the growth kinetics of TiC strings using a combination of a hot-wall CVD reactor and an Ar^+ laser.

The aim of this work was to study the formation of TiC films on D2 steel specimens and miniature tools using a 100

W CO₂ laser and a gas mixture of TiCl₄/CCl₄/H₂/Ar. Emphasis was placed on the application of the technique on real industrial tools in order to demonstrate its future potential.

2. Experimental details

2.1. Substrate materials

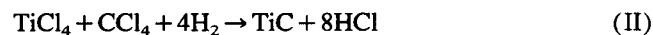
The substrate that was used for deposition of TiC was a tool steel D2 according to AISI with chemical composition 1.55% C, 0.27% Mn, 0.4% Si, 11.34% Cr, 0.53% Mo, 0.24% V. Samples of D2 steel were cut from a rod 50 mm diameter. The specimens were heat treated as follows.

- Preheating: 15 min, 600 °C.
- Austenitizing: 1 h, 1020 °C.
- Quenching in oil: 1 h, 50 °C.
- Tempering: 1 h, 500 °C, air cool.
- Tempering: 1 h, 500 °C, air cool.

The hardness after the tempering treatment reached the value of 63 RC. Prior to deposition experiments, the surface of the specimens were ground to a 600 grid with SiC paper and cleaned with acetone/ethanol in an ultrasonic bath. The substrates used in the experiments were either rectangular (10 mm × 10 mm × 5 mm) or cylindrical (∅ mm × 10–20 mm length).

2.2. Precursors and reactions

A thermodynamic analysis of the TiC formation from gaseous precursors TiCl₄, CH₄ or CCl₄ and H₂ was performed in order to calculate the heterogeneous equilibrium reaction pressures and temperatures. The Thermo-calc thermodynamics software system employing was used [10] of the SGTE (Scientific Group Thermodata Europe) pure substance thermochemical databank. The analysis involved the calculation of the free energy difference (ΔG) for the reactions:



The value of ΔG was calculated as a function of temperature as shown in Fig. 1.

Considering that the total pressure was 5 mbar, it was found that the temperature at which the reaction is thermodynamically feasible is lower in the case of TiCl₄/CCl₄/H₂ (400 K) than in the case of TiCl₄/CH₄ (800 K) as precursor gases. Therefore it was decided to use CCl₄ as a carbon source, in order to reduce the deposition temperature. In the case that atomic hydrogen was used the reaction temperature is much lower. The LCVD process was based on reactions (I)–(III) above.

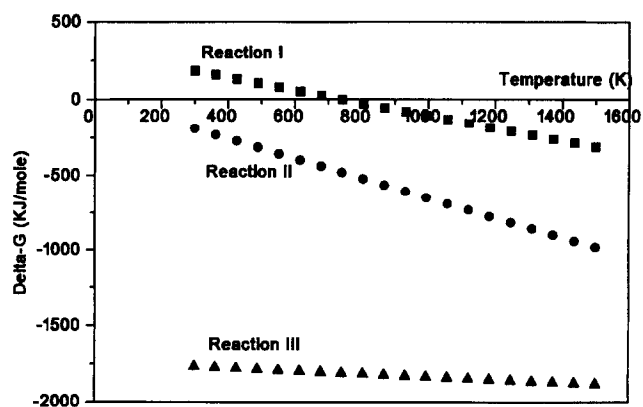


Fig. 1. Gibbs free energy change versus temperature for reactions (I), (II), (III).

2.3. Apparatus and processing

A schematic diagram of the LCVD reactor is shown in Fig. 2. The r.f. excited CO₂ laser, with transmission electron microscopy TEM₀₀ mode and maximum power 100 W at a wavelength of 10.6 μm , was incident at 45° angle to the substrate. The 1/e² spot size at the laser exit was 4 mm, and was focused using a ZnSe lens. Power density was controlled in the region of 1 000–17 000 W cm⁻². Both laser entrance windows were flushed with Ar during the deposition process.

The TiCl₄ and CCl₄ in the liquid phase were heated inside glass containers/bubblers at 40–50 °C. The carrier gas, Ar, was passed through the TiCl₄ and CCl₄ bubblers and the resulting gas–vapor mixtures were passed through reflux coolers maintained at steady temperatures of 30 °C, this system ensured that the degree of saturation of the carrier gas is 100%. The reactant gas supplies were thus controlled by the cooler temperature and the Ar mass flow rates adjusted accurately by means of mass flow controllers.

A simple atomic hydrogen source has been built in order to produce reactive atomic hydrogen by thermal dissociation of H₂ [11,12]. The source consisted of a small water-cooled cylindrical stainless-steel chamber which contained a W filament shaped in a coil form. Molecular H₂ presents a significant degree of dissociation at 1400–2300 °C under the catalytic action of W at pressures below 1 Torr, despite the high binding energy of the H₂ molecule. This device was used in most of the experiments as it was proved effective in eliminating Cl contamination of the deposited layers. Before

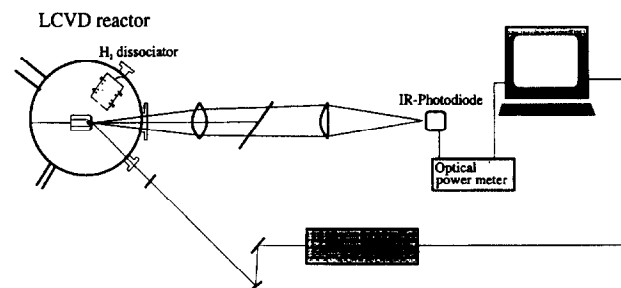


Fig. 2. Experimental set-up for LCVD processing method with the feedback loop system.

Table 1
Experimental conditions for the CO₂ laser and the gas supply system

CO ₂ laser	
Power density	1 000–17 000 W cm ⁻²
Repetition rate	5 KHz
Duty cycle	20–90%
Precursors	
Flow of carrier gas Ar for the TiCl ₄	100 sccm
Flow of carrier gas Ar for the CCl ₄	10 sccm
Partial pressure of H ₂ /H	5 mbar
Total pressure	8 mbar

the introduction of the reaction gas mixture, the reactor was evacuated to a pressure of 10⁻⁵ mbar.

In the pyrolytic LCVD the substrate temperature is the dominant factor of the deposition growth rate. The temperature depends on the heat source, i.e. the CO₂ laser power, the reflectivity of the substrate at the laser wavelength, the reflectivity of the coating, the thermal conductivity of the substrate and the coating and finally the power losses due to convection and radiation of the substrate. Additionally, at the early stages of the deposition the absorption coefficient of the substrate changes considerably due to multiple reflection of the laser beam in the microcavities formed by microstructure grown during the LCVD. The critical role of the temperature created the need to control it during the deposition. An infrared pyrometry system was used as the sensor of a PC-based feed back loop system that controls the CO₂ laser power (Fig. 2). An estimation of the temperature was performed by measuring the IR emission from the hot spot created by the laser beam on the sample. The IR emission was collected and focused onto an IR photodiode. The photodiode analog signal was fed to an A/D interface card installed in a PC microcomputer. The program compared the digital signal with a desired value and controlled accordingly the timer-counter card which triggered the CO₂ laser power by comparing the measured temperature with the desired value.

Table 1 shows the range of experimental conditions used in the experiments discussed in the next section.

2.4. Film characterization

The morphology of the films was studied with optical as well as scanning electron microscopy (SEM). Surface chemical analysis was performed using energy dispersive X-ray analysis (EDAX). The composition of the coatings was also analyzed with X-ray diffraction, in order to identify TiC peaks. Finally, extraction replica were prepared for imaging and electron diffraction in the TEM. The hardness of the films was measured using a Vickers/Knoop microhardness tester. Hardness measurements were performed as a function of applied load.

3. Results and discussion

Initial experiments performed with the rectangular samples and without the use of the feed-back loop system and the

atomic hydrogen source, resulted in films grown both inside and outside the irradiated area with variable thickness and morphology. A typical result is depicted in the SEM photograph of Fig. 3. There is a melted central region where EDAX analysis showed low Ti concentration, surrounded by an annular area, where a 3 μm thick film was deposited, exhibiting high Ti presence. Further away from the central area the Ti presence is again minimized and a Cl-rich phase appears.

TEM was used to determine the phases present in the annular region of the film. Samples were taken by extraction replica and were examined after suitable preparation. The dominating phase detected had an fcc structure with a lattice constant of $a_0 = 3.87 \text{ \AA}$, while the theoretical value for TiC is 4.32 Å; it can be deduced that the phase detected was non-stoichiometric TiC (TiC_x). Other phases present in the film had very large values of a_0 , characteristic of compounds such as TiO₂ or TiCl_x which were also detected by XRD analysis.

All subsequent experiments were performed with the feed-back loop system and the atomic hydrogen source. The former eliminated the local melting of the sample while the latter minimized the presence of Cl in the films. Cylindrical samples with a diameter of 5 mm and 10–20 mm length were irradiated on the flat face. The modified temperature profile on the surface as well as the small size of the irradiated area led to the development of uniform crystalline films with a particle-like morphology (Fig. 4). The film thickness was within the range of 1–3 μm and covered all the flat surface without any sign of the laser spot which was less than 1 mm. The deposition rate was estimated around 1 μm min⁻¹. EDAX analysis showed significant presence of Ti all over the film and virtually no Cl. TEM analysis (Fig. 5) revealed the presence of TiC with a lattice constant $a_0 = 4.20 \text{ \AA}$, very close to the theoretical value of 4.32 Å. Bright- and dark-field images (Fig. 6) showed that the film had a fine dense structure and their crystalline size were of the order of nanocrystals (10–250 nm).

Knoop microhardness measurements were performed using a load of 25 g. For higher accuracy the diagonal meas-

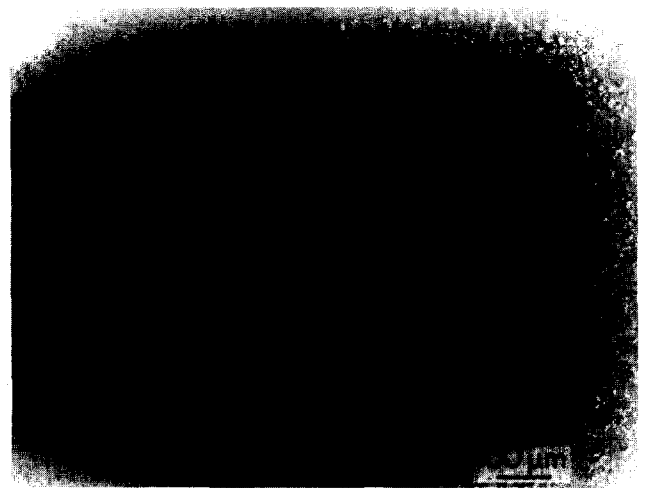


Fig. 3. SEM photograph of the film deposited on the rectangular sample.



Fig. 4. SEM photograph of the film deposited on the flat surface of the cylindrical sample.



Fig. 5. Diffraction pattern of the fcc structure ($a = 4.20 \text{ \AA}$).

Measurements were carried out in the SEM and values of around 2000 HK were found. The TiC hardness value is 2800 HV [1] and the reduced measured values can be attributed to the substrate influence which, as thermally treated D2 tool steel, exhibits a value of 500 HV. Another important factor for the film characterization is the adhesion strength. In the present case no spallation was observed around a Rockwell C indentation, which led us to the conclusion that the adhesion was moderate.

The bulk substrate material was carefully examined in terms of both microstructure and hardness; these tests showed that no material degradation had been caused during the deposition process. Metallographic analysis of the deposited substrate was carried out in order to examine the possibility of heat-induced damage on the D2 steel substrate by the laser treatment. It was observed that overaged carbides are not present in the treated area. The bulk microhardness of the D2 steel remained unaffected as it is detected from the depth profiling microhardness measurements. EDAX analysis showed a significant presence of Ti all over the film and virtually no Cl. TEM analysis revealed the presence of TiC with a lattice constant $a_0 = 4.20 \text{ \AA}$, compared with the theo-

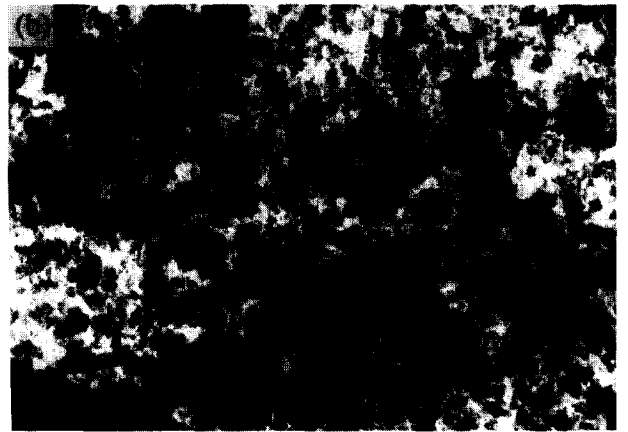
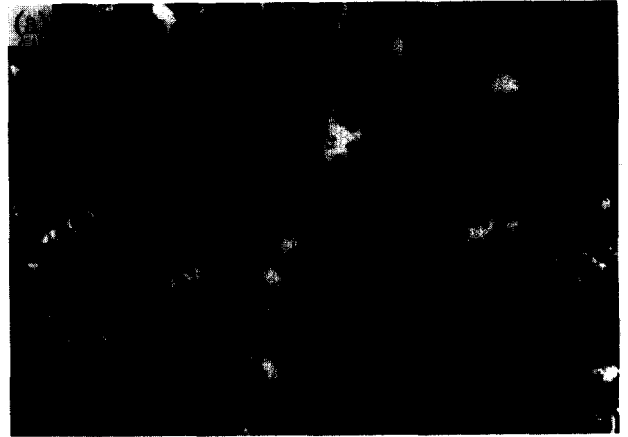


Fig. 6. Dark- and bright-field image (TEM) SPN1447.

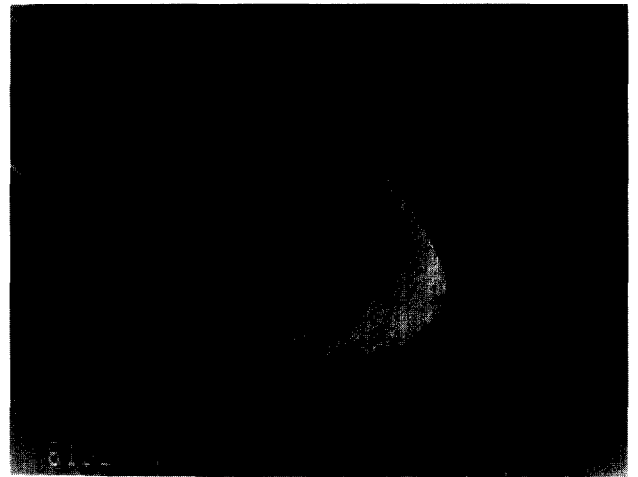


Fig. 7. SEM photograph of the textile needle after TiC deposition.

retical value of 4.32 \AA . Bright- and dark-field images showed that the film had a fine dense structure and their crystalline size were of the order of nanocrystals (10–250 nm).

The next series of experiments was performed with real industrial tools and more specifically needles used in the textile industry. These tools suffer from wear due to the cotton thread passing at high speeds through their holes. The laser spot was focused on the needle hole and the optimized result is depicted in the SEM photograph of Fig. 7. The film was found to be near-stoichiometric TiC with microhardness val-

ues of around 2500 HK. The deposition rate was estimated around $7 \mu\text{m min}^{-1}$. The deposited layer covered not only the area around the hole but all the curved surface of the needle; moreover, the specific sample selected for deposition was heavily worn and the damaged area was partly repaired. This shows the potential of this technique for repairing miniature tools.

4. Summary and conclusions

TiC layers have been successfully deposited locally on D2 tool steel specimens with the aim to improve their mechanical and chemical surface properties. The deposition process was based on a pyrolytically-induced chemical reaction of TiCl_4 and CCl_4 compounds combined with an atomic hydrogen source. Local heating of the substrate was achieved by means of a 100 W CO_2 laser controlled by a microcomputer-based feedback loop system, involving on-line substrate temperature monitoring. SEM/EDAX, XRD and TEM techniques showed that the films consisted of stoichiometric TiC with an fcc structure and a lattice constant of 4.2 \AA , exhibited structural uniformity and moderate adhesion and had a thickness of 1–3 μm . Microhardness values were found in the range of 2 000–2 500 HK, compared with the 500 HV hardness of the tempered D2 tool steel.

The application of the present method for the local deposition of TiC on miniature industrial tools resulted in uniformly covered curved surfaces around the irradiated area. This suggests that the LCVD technique can produce protective films with good properties on sensitive areas of small

three-dimensional tools and improve their work life and reliability.

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