

# THE EFFECT OF PERCENTAGE CARBON ON THE CVD COATING OF PLAIN CARBON AND LOW ALLOY STEELS

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## ABSTRACT

Two steels En 3 and En 39 were given a TiC-TiN CVD coating in the carburized and uncarburized conditions. The continuity of the coatings and their adherence to the substrate were examined. The thickness of the deposited coatings were also measured, their adherence to the substrate and their thickness was affected by the percentage carbon of the substrates surface. Moreover it was found out that there exists a marked difference between the coatings deposited on the two steels.

## INTRODUCTION

Chemical Vapour Deposition is a relatively recent development in coating of (CVD) surfaces of metals for the purpose of increasing resistance to various forms of wear.

The coating materials' list currently under use includes: Carbides of Ti, Cr, Si, Ta, W, V; Nitrides of Ti, Al, Cr; Oxides of Al, Cr, Nb, Ta, Ti, V and others which are mostly coated on tool steels and cemented carbides<sup>[1]</sup> and number of non metallic materials. Of these coating substrate systems which have attained industrial importance, the coating of TiC and/or TiN on tool steels and cemented carbides are the first to be used with achievements of increased tool life up to twenty times<sup>[2,3]</sup>

### CVD Process

The conventional CVD process involves the continuous admission of reactant gases into a heated chamber containing the substrate whereby the gases react at the vicinity of or on the substrate to produce a solid deposit. The main parameters affecting the process are temperature pressure and concentration of the chemicals. These together with other parameters need to be controlled firstly to ensure that the reaction takes place in the vicinity of or on the substrate and secondly to optimize the process.

The various thermochemical reactions in use for the coating substrate systems in practice fall in one of the following.

1. Thermal deposition reaction  
Eg.  $Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g)$
2. Reduction reactions  
Eg.  $WF_6(g) + 3H_2(g) \rightarrow W(s) + 6HF(g)$
3. Displacement or exchange reaction  
Eg.  $CrCl_2(g) + Fe(s) \rightarrow Cr-Fe \text{ alloy} + FeCl_2(g)$
4. Disproportionation reaction  
Eg.  $2GeI_2(g) \rightarrow Ge(s) + GeI_4(g)$

### Process Parameters

The structure of the deposited coating, its continuity and adherence to the substrate are mainly determined by the temperature and the partial pressures of the reactant gases. According to the general theory of vapour deposition, the effect of temperature and partial pressures will depend on whether the reaction is exothermic or endothermic.

In most CVD processes where the reactions are endothermic an increase in temperature increases the supersaturation of the product in the gas phase which also increases with increasing partial pressures of the reactant gases. The result of increased temperature and pressure would then be, the deposition of coarse grained coatings which in severe cases may show epitaxial growth of the deposits. Coatings produced under such conditions though thick, continuous, and adhered to the substrates, do not increase service life of tools<sup>[4]</sup>.

### Adherence of Coating

One of the requirements for a successful CVD coating is the adherence of the coating to the substrate. This is generally determined by the process parameters mentioned above, the nature of the coating-substrate system, the reactant and by product gases.

A large number of materials may be deposited by CVD on various substrates and quite a few have alternative gaseous reactants. However the number of coating and substrate materials which form compatible systems to the extent of industrial application is limited.

Gaseous reactants, in addition to producing the material to be deposited are preferred to have a by product which does not attack the substrate.

In addition to requirements to be met individually, coating and substrate CVD systems must have only a limited variation in their coefficients of expansion and further more should be pairs which are bounded metallurgically.

Coating materials must have the necessary properties such as hardness, low coefficient of friction, resistance to galling, wear resistance and the required degree of adherence. Often, all the required properties may not be obtained from a single coating material and thus a double layer may be employed.

Substrates are also required to have a number of properties. These are a reasonable hardness to support the coating materials, the existence of ample nucleating sites for the deposit so as to ensure a continuous, uniform and tightly adhered deposition of the coating and to maintain these requirements irrespective of the temperature cycle which the CVD process undergoes.

Carbide tools and tool steels in general meet the requirements of substrate materials and are thus used in a number of applications coated with various materials. Further application of the process to substrate materials such as plain carbon and low alloy steels, which undoubtedly would have opened wider application, did not materialize due to the absence of some of the requirements.

Carbides met the hardness requirement and nucleation is highly facilitated on the cobalt binder<sup>[2]</sup>. Tool steels have to be given a post coating hardening and as regards to nucleating sites the metal carbides were found effective<sup>[5]</sup>.

In plain carbon and low alloy steels one possible and economical means of imparting the main substrate materials requirement i.e. hardness and nucleation sites is by a carburizing treatment. High surface carbon in addition to possibly producing enough metal carbides, can result in the required hardness by post coating hardening.

This paper presents and discusses the results, obtained from a first attempt towards successful deposition of TiC-TiN coatings on plain carbon and low alloy steels.

## MATERIALS AND EXPERIMENTAL METHODS

Steels En 3 and En 39 (for compositions see Table 1) of about 25 mm diameter of different surface carbon content were coated with a TiC-TiN double layer. The different surface carbon contents

were achieved by carburizing a number of samples of each steel in an Ipsen RT25E sealed quench furnace equipped with temperature control and carburizing gas flow regulators followed by grinding the specimens on one surface only, to a pre-determined depth which corresponds to a surface carbon content. Optical emission direct reading spectrometry E1000 series Polyvac was used to produce carbon profiles of samples of both steels after being carburized together with the rest of the samples.

The TiC-TiN coating process was done together with carbide tool steels in one of manufacturing plants in U.K. and hence details of the process were not disclosed. However it was known that the process didn't have major variations with currently accepted general process of TiC-TiN deposition techniques. Below is a schematic representation of the furnace and general descriptions.

In the production of TiC coating,  $TiCl_4$  with Hydrogen as a carrier gas and  $CH_4$  as the hydrocarbon reactant are supplied to the furnace maintained with inert atmosphere heating. Reaction of  $TiCl_4$  with  $CH_4$  on the substrate surface produces TiC deposits.



In TiN coating  $CH_4$  is substituted by Nitrogen or ammonia.

In a double layer coating of TiC/TiN,  $CH_4$  is gradually substituted by  $NH_3$  or  $N_2$  resulting in a transition coating of Titanium Carbonitride layer.

In both stages the HCl by-product is neutralized by NaOH in the scrubber.

Figure 2 below shows the temperature cycle with time for the above process.

TiC-TiN CVD coatings produced as above were given visual inspections, and the thickness were measured. Further more the samples were given microscopic examinations.

## RESULTS AND DISCUSSION

Visual examinations of the samples after the treatment revealed that a continuous deposit was achieved on all samples. However uncarburized samples of both steels and those surface with low carbon contents showed noticeable flaking-off deposits during microstructural sample preparation.

Table 1. Compositions of steels En3 and En 39

Steel	%C	Si	S	P	Mn	Ni	Cr	Mo
En 3	0.230	0.206	0.207	0.019	0.540	0.220	0.132	0.036
En 39	0.150	0.274	0.013	0.019	0.372	4.12	0.140	0.227

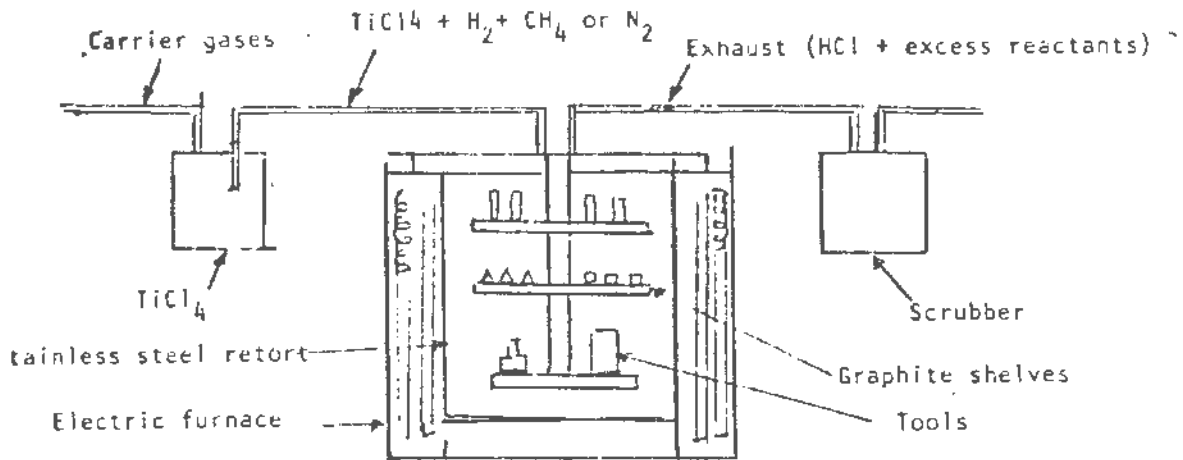


Fig.1 Schematic representation of CVD process for TiC and TiN coating. From scientific coating<sup>5</sup>

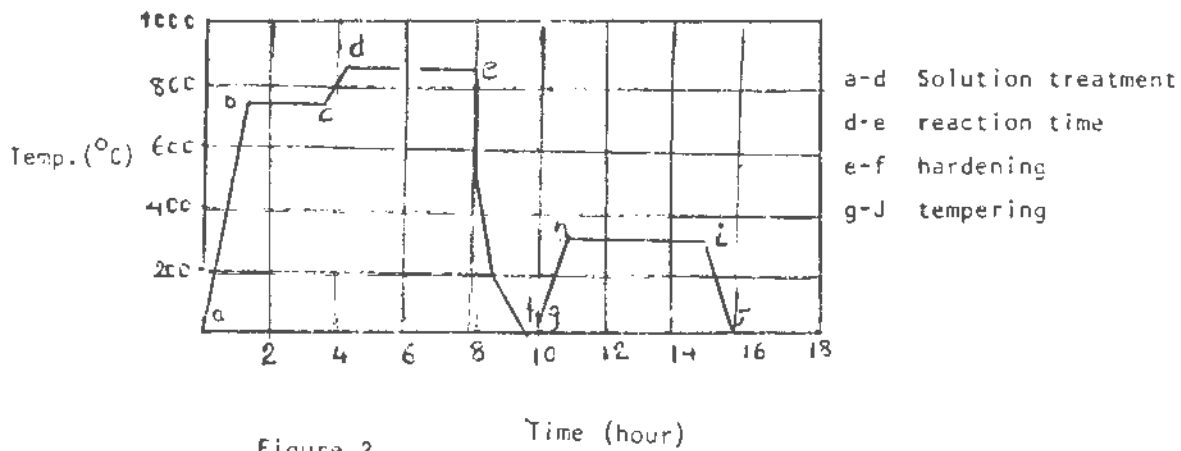


Figure 2

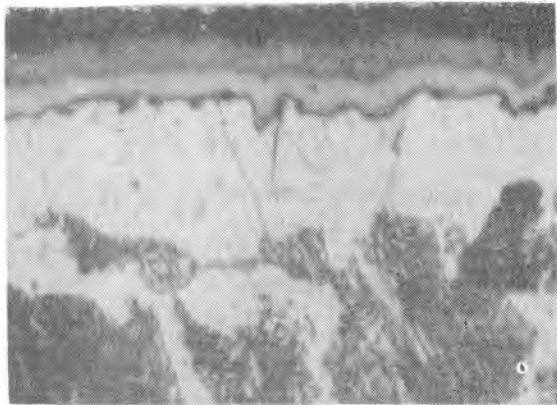


Fig.3 Micro structure En 3 steel x 800 carburized to 1% C on the surface before coating. Coating consists of TiC, transition  $TiC \times N_{1-x}$  and TiN



Fig.4 Microstructure of En 3 steel x 400. CVD coating on 0.43% at the surface.

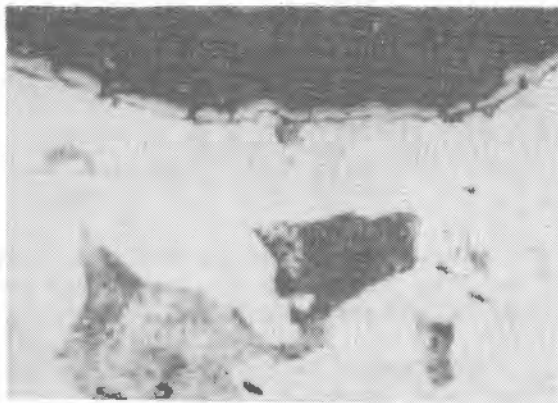


Fig.5 Microstructure of En 3 steel x 400 CVD coating on uncarburized 0.22%C surface Note the discontinuity on the surface

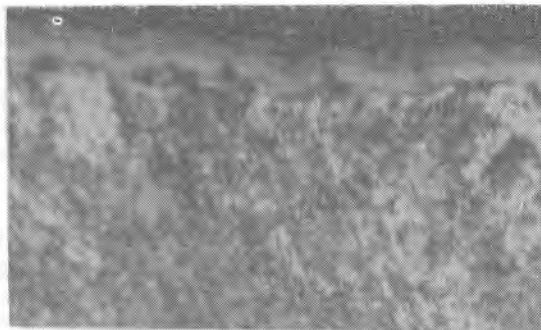


Fig.6 Microstructure of En 39 steel x 800 CVD coating on 0.75%C Note the slight decarburization.

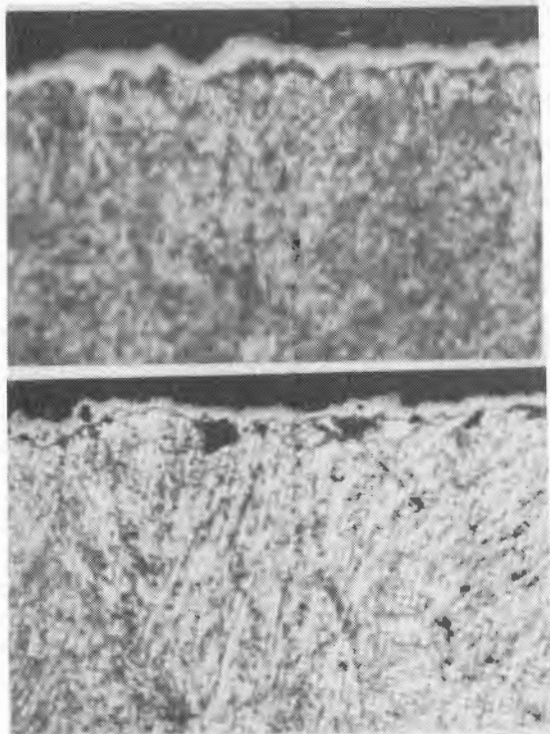


Fig.7 Microstructure of En 39 steel x 400. CVD coating on 0.43% at the surface

Fig.8 Microstructure of En 39 steel x 400. CVD coating of uncarburized 0.15%C. Coating is of irregular thickness.

Flaking-off of uncarburized and low surface carbon content samples even during sample preparation are measures of an almost non-existent adherence which arises due to insufficient nucleating sites on the substrate. Initially observed continuous deposit in these samples must have been achieved by side-wise growth of the coating.

Microstructural observation done on all samples (Fig. 3-8) revealed the discontinuous nature of the coating on the grinded surface. Characterized by low carbon content, and the continuity of the coatings on high carbon surfaces. The contrast is to be expected due to two possible reasons. The first is that the higher percentage carbon on the surface resulted in a direct reaction of the substrate surface with  $TiCl_4$  gas forming nuclei on which subsequent deposition was facilitated. This possibility is supported by observed highly carburized surfaces of the samples (see Fig. 3-6). The second possibility with more weight for En 39 steels is the availability of metal carbides even at the higher process temperatures which as described in reference 1 must have acted as nucleating sites.

Pronounced discontinuity of coating as in uncarburized En 3 steels may in addition to insufficient nucleation suggest possible substrate attack by gaseous by-products. Generally the necessary condition for substrate attack is a negative Gibbs free energy change ( $\Delta G$ ) for the reaction.



where Gibbs free energy change  $\Delta G$  is given by

$$\Delta G = \Delta G^\circ + RT \ln \frac{P_{H_2}}{P_{HCl}^2}$$

Where  $\Delta G^\circ$  is the standard free energy change and  $P_{H_2}$  and  $P_{HCl}$  are the partial pressures of  $H_2$  and  $HCl$  respectively.

The details of the CVD coating process have not been disclosed. However if conditions were favourable for substrate attack then high surface carbon content samples would have reduced the activity of  $Fe$  while low carbon surface would have not done so. Takahashi<sup>6</sup> et al as referred in reference 7 which has dealt with substrate attack of by-product gases have observed that  $Fe$  is readily attacked by  $HCl$  gas.

Scanning electron microscope observations (not shown) done on samples corresponding to Figure 3 and 6 revealed the existence of pores at the interface of the coating and the substrate in both samples. The origin of these pores may be due to diffusion of carbon out-wards. Another possibility is a minimized substrate attack which will leave nucleated sites which latter end up as pores.

Table 2. Coating thicknesses of TiC and TiN on En 3 (surface carbon initial 1.0%)

No.	Depth below Carb. surface (mm)	Corresponding C%	Thickness of layers ( $\mu\text{m}$ )		Thickness of layer on the carburized Surface ( $\mu\text{m}$ )	
			TiC	TiN	TiC	TiN
1.	0.1	0.97	4.0	3.0	4	2.5
2.	0.2	0.82	2.5	1.0	2.5	2.0
3.	0.3	0.66	4.0	3.0	5	3.0
4.	0.4	0.53	3.0	2.0	4	2.0
5.	0.5	0.43	3.0	2.5	3.5	2.0
6.	0.6	0.35	2.0	0.8	3.0	2.0
7.*	0.08	0.96	3.0	1.15	4.0	2.5
8.**	-	0.22	2.5	2.0	-	-

\* Sample air cooled after carburizing

\*\* Uncarburized sample with base carbon content of 0.22%

Table 3. Coating thickness of TiC and TiN on En 39 (initial surface carbon 0.75%)

No.	Depth below carb. surface (mm)	Corresponding C%	Thickness of layers ( $\mu\text{m}$ )		Thickness of layer on the carburized Surface ( $\mu\text{m}$ )	
			TiC	TiN	TiC	TiN
1.	0.1	0.66	2.2	1.8	3.5	2.0
2.	0.2	0.53	2.0	3.0	5.0	3.0
3.	0.3	0.43	4.0	2.0	3.0	2.0
4.	0.4	0.34	1.8	1.5	2.5	1.5
5.	0.5	0.28	2.8	1.5	2.5	1.5
6.	0.6	0.23	2.2	2.0	4.5	2.5
7.*	0.08	0.68	2.0	1.5	2.0	2.0
8*.	-	0.15	1.7	1.5	1.8	1.7

Coating Thicknesses of Deposites were measured for all samples. The values presented in Tables 2 and 3 are averages of large number of randomly measured values with a minimum of 10 readings in each case.

The results in Table 2 and 3 show that despite some variations there exists a strong relation between the surface carbon content and the thickness of the deposited coatings. Those surfaces with higher carbon contents have acquired thicker deposites. The above relation is further justified by the fact that almost all the coatings on the carburized samples (last column of the tables) attained thicker coatings where as the uncarburized samples had thinner and discontinuous coatings.

Comparison of the thickness of the coatings developed on the two steel samples shows that there is only a slight variation, with the *En 3* samples coating being a bit thicker than the *En 39* samples coatings (see the last two columns of the tables).

Decarburization and subsequent reaction of carbon with *Ti* seems to be prominent on *En 3* steels. On the other hand decarburization is very small in *En 39* steel samples and thus nucleating sites must have been offered mainly by the metal carbides. Of the two mechanisms each predominant in each steel, decarburization in *En 3* steels is more effective than metal carbides in *En 39* steels.

The thickness of coatings is only one aspect of the successfulness of the deposition process. Infact while this can be achieved by increasing time and changing process parameters<sup>4</sup>, it is the structure of the deposites and their degree of adherence to the substrate, which is more effective as far as increased service life of tools<sup>8,9</sup> is concerned.

No direct measurement and observation have been made to determine the structures of the deposites and as such no discussion can be presented concerning structures and expected service properties.

### CONCLUSIONS

1. Depositios of reasonable thickness and continuity can be made on carburized plain carbon and low-alloy steels.
2. From the limited tests done better coatings are obtained on substrates with higher carbon contents. Those surfaces with higher carbon content have achieved thicker coatings with higher degree of continuity and adherence to the substrate as compared to substrates with low carbon surfaces.

3. Comparison of *En 3* and *En 39* steels shows that while there is hardly and difference in the coating thickness attained there is a difference of the nucleation mechanism in the two steels possibly leading to structural variations of the deosites in the two steels.
4. Further investigations on the degree of adherence and the structure of the deposit is required in order to forward a definate remark as to the possibility of using plain carbon and low alloy steels with CVD treatment.

### REFERENCES

1. K.K. Yee. Protective Coatings for metals by CVD, Int. Met. Reviews 1978, No. 1, P. 19.
2. Berna A.G Olten, Industriestr. Hard Coatings for improved life, Metallurgia, April 1982, P. 160.
3. R.Milovic, E.F.Smart, M.I.H.Wise, Comparison between use of *TiN* Coated and Uncoated high speed steel and fine grained cemented carbide tools in cutting of resulphorized 0.08 Wt%C free cutting steel, Mat. Sci. & Techn. Jan. 1986, Vol. 2, P. 59.
4. John r.Peterson, partial Pressures of *TiCl<sub>4</sub>* in CVD OF *TiN*, J.Vac. Sci. & Tech. Vol. 11, No. 4 July/August 1974, P. 175.
5. Mark Podob, CVD hard coatings lengthen tool life, Metals, progress, May 1982, P. 50.
6. T.Takahashi et al, J. Electrochem. Soc. 114, 1230 (1967).
7. W.A. Bryant, Factors affecting the adherence of CVD coatings, J.Vac. Sci. Tech. Vol. 11, No. 4 July/August 1974, P. 719.
8. W.Schintlmesister et al, structure and strength effects in CVD *TiC* and *TiN* coatings, J.Electrochem Soc. Vol. 123, No. 6 June 1976 P. 924.
9. V.K.Sarin et al, The effect Eta of phase on the properties of CVD *TiC*-coated cemented carbide cutting tools, J.Electrochem. Soc. Vol. 126 No. 7, July 1979, P. 1280.