COATINGS SYSTEMS: CHROMIUM CARBIDE, NITRIDE AND CARBONITRIDE

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ABSTRACT

The process of the chemical deposition from vaporous implies the adsorption of the mobile atoms (monomers) on the substrate surface, their migration with embryos and stable nucleus formation, followed up by further growth through the adsorption of new atoms on the surface and also by the nucleus coalescence. The final structure of the deposed layer is given by various effects such as, the adsorption of impurities, the incorporation of gaseous, the co-deposition of another elements, the crystallization, etc.

The ultimate properties of the coatings are further dependent on the nature and composition on the substrate. Therefore, in theory a vast number of substrate-coating combinations is possible, with its own set of physical and chemical characteristics.

If the vapor chemical deposition takes place within a tubular continuous reactor, a gas carrying the reacting species is passed over the substrate. At the substrate surface, the reacting elements undergo a number of chemical reactions leading to the product formation. Part of the products are deposited on the substrate and part of it goes back to the gas stream [1].

Before examining the vapor chemical deposition reactions it must be determined if the reaction is possible thermodynamically, if the calculated concentrations (partial pressures) of the reactants under equilibrium conditions are less than their initial values.

KEYWORDS: chemical vapour deposition, substrate-coatings, nitride, carbonitride, chromium carbide

1. Introduction

The basic phenomen of chemical vapour deposition (C.V.D) has been known for centuries in the pack carburizing of iron, although it may not have been recognised as a gaseous or vapour phase process. Indeed the term C.V.D. has, of late, achieved the characteristic of being something of a new process a recent development, particularlywith the application to metal woeking tools of coating of TiC and TiN.

Whether the process is carried out by the long established pack cementation technique or by the more recent, but still well-known, totally gaseous technique, the basic process is still C.V.D. Indeed, to those working with these processes the use of liquid baths is included within the generic term, because the coatings of a given type have such similar properties whichever method is used [1] – [2].

The general characteristics and process techniques of pack, purely gaseous and liquid methods of introducing one element into the solid surface of another, are well known through the very widespread use of the carburization of steel and iron components.

The introduction of elements other than carbon is achieved by using similar techniques. The characteristics exhibited by these coatings result from the differing chemistry of elements involved.

To that end, and before dealing with specific exemples, it is worthwhile to examine some of fundamental differences between the processes used for surface coating.

2. Chromium Carbide

Chromium carbide coatings with a hardness of about 2000 D.P.N. are particularly successful in sliding wear applications, the most often quoted example being the bicycle free-wheel (fig.1).

The life time of the smoll bodies which rotate to lock and unlock the free-whell device can be increased about 20 times for only a small increase in cost. Many textile machine parts have been similarly coated.

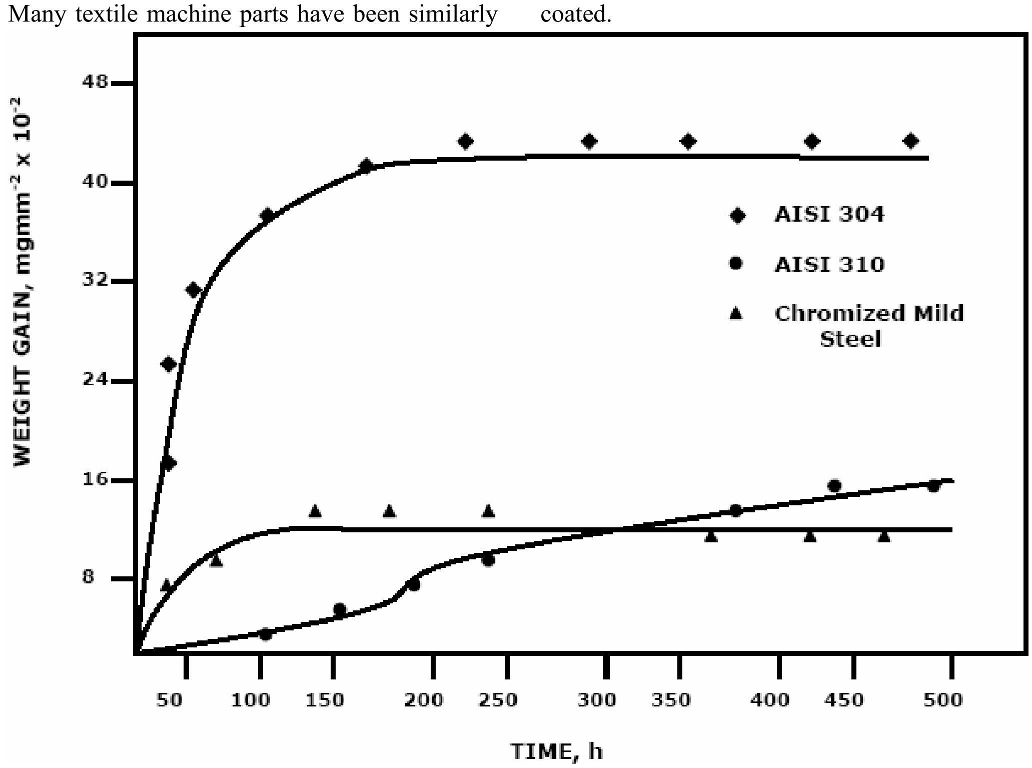


Fig.1.*The oxidation resistance at 1000^{o}C in air of chromized mild steel wowen wire (0.25 mm wire diameter) as compared with wowen wire samples of austenitic stainless steels.*

3. Titanium carbide. Nitride carbonitride

Overlay coatings consisting of TiC, TiN and TiC/TiN either separately or as a bonded structure are very widely used on throw-away indexable carbide inserts. TiC and TiN are isostructural and can be formed in continuous solid solution of any composition. These coatings give a surface hardness of around 3000 D.P.N. and their use on carbide containing substrates has simplified the range of carbide compositions necessary to cover all cutting applications.

The properties of TiC and TiN appear to compliment each other in providing resistance to both the slid in wear and crates wear observed on carbide cutting inserts.

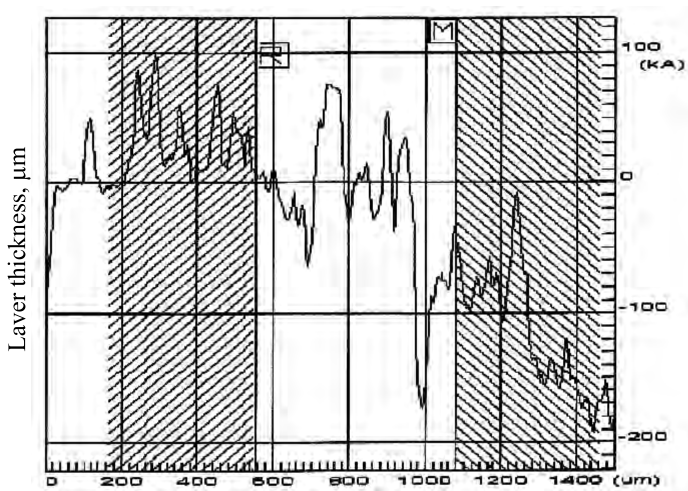
The key to their wear resistance on cutting tools is their chemical inertness as well as their hardness. They have no tendency to react with the extremely clean, oxide free, surface of the swarf as it passed the cutting tool. The TiC/TiN combination of coatings is also on carbide forming tools, for example deep drawing dies. The chemical inertness of the coating is important here to reduce tendency for cold welding to occur.

Steel cutting tools been coated with TiC/TiN but with less success than carbide tools. This is caused partly by the lower hardness of the steel substrate which provides less support for the coatings and partly by the necessaty to re-harden steel substrates after coating.

The latter feature is necessary as the C.V.D. process temperature for TiC and TiN is around 1000^{o}C. With some steels this re-hardening can be combined with the coating cycle, but in most cases a separate vacuum heat-treatment step is required [3]-[4].

TiC coating alone on steel forming tools have been very successful. In this case there appears to be very little advantage in the TiC/TiN combination. All types of punch and die combinations have been coated with TiC to give increased wear life and better surface finishes on the product.

Tool for powder metallurgy have been coated withboth TiC and TiN. In this case the coating act as release agents by reducing the tendency for powder compacts to bond to the tools (fig.2)



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Meas. Range ...655 KA
Profile ....Hills&Valleys
R. Cursor ....6644A @ 554.35um
M. Cursor ..... -38513A @ 1080.43um
Vert. Delta .... -45157A
Horiz. Delta 526.09um
ANALYTIC FUNCTIONS:
R:um   M:um
Film thickness = 8,5 E + 4A = 8,5 µm

Fig.2. *Surface profilmeter measurement of the thickness of TiC film for 4 h exposure time.*

The choise of the substrate steel is important in the use of TiC and TiN coatings. The TiC coating forms most adherently on steelswith a carbon contecnt over 1%, while TiN is less influenced by the composition of the substrate [5]-[6] .

High speed steels have been used for coating cold forging dies with relatively low dimensional tolerances. For high precision parts where distortion on re-hardening must be minimised.

4. Titanium Nitride

Titanium nitride is a yellow coloured material, and when polished resembles gold. The resemblance can be improved by careful control of the stoichiometry and also by adding traces of carbon. This has caused titanium nitride to be considered for various decorative applications [7].

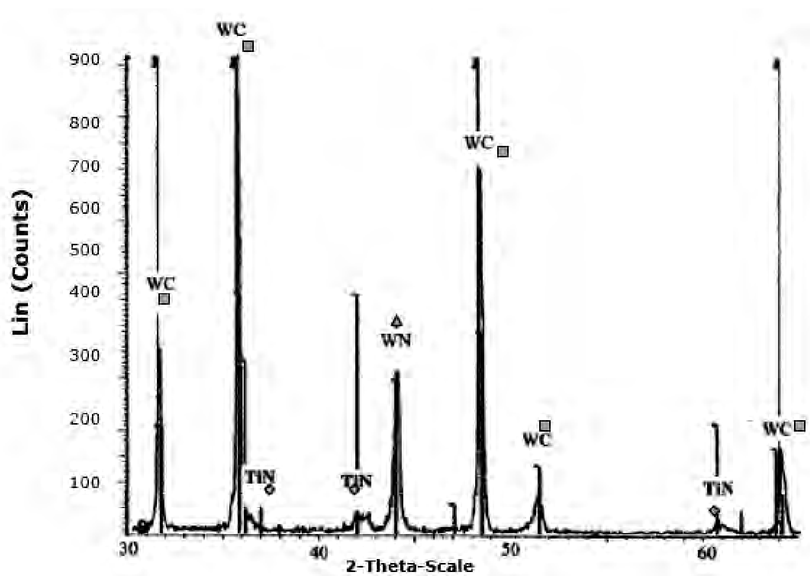

Fig.3. *XRD pattern of nitride thin layer for 4 h exposure time.*

Watch cases, particularly those made from sintered tungsten, on coated with titanium nitride, and there have been investigations on less expensive items of personal jewellery, cigarette and pens. The hardness of titanium nitride is very suitable for these applications and also its corrosion resistance is adequate for it to maintain a bright appearance even when constantly handled. The largest technical barrier to thewidespread use of C.V.D. titanium nitride as a decorative coating is the necessity to polish the C.V.D. layer. Unless coated parts are designed so that can be polished automatically in large numbers, the cost of polishing is often prohibitive (fig.3).

5. Conclusions

An attempt has been made to highlight some specific cases where C.V.D. coatings have been able to extend the useful life of components used in various industries. It is not always the case that standard processing conditions can be applied to solve the presented problems on any given component. There could be many facets to the problem wich require special alternation to the coating conditions (variations in processing time, temperature, special jigging etc.).

Of the types of coating systems examined, only a few have been developed for practical application. This is in part related to the high coast of coling up specialist plant and the problems of efficient utilization of this plant when operated by a service industry [8] .

Tables 1 some of the C.V.D. coating available commercially along with their typical applications.

An important advantage of the plant used for producing C.V.D. coating is its versatility. It is possible, using the same basic equipment, to alter operating conditions and produce coating of different compositions and characteristics [9].

Table no. 1 *The C.V.D. coating*

Coating material	Typical substrates	Substrate improvements	Typical components
TiC	High speed steels, sintered carbide and tool steels	Wear	Sintered carbide cutting tips, steel press tools, punches and dies.
TiN	As for TiC	Wear, Corrosion	As for TiC and also decorative parts
SiC	Graphite	Oxidation	Heater elements

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