New and Environment-Friendly Methods in Surface Treatment (CVD, Plasma Assisted CVD, PVD, Ion Implantation)

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Abstract

When discussing new surface treatment processes and tribological surface treatments and coatings for tools and wear parts the focus is traditionally only put on the potential longer life time of the tools and the wear parts. Longer life time is by far not the only issue of relevance in this context. In this article it is pointed out that there are a row of other very important gains to be won by the relatively new so-called dry coating processes. The processes are environment-friendly themselves. Tools that have been surface treated with the processes can give higher productivity, better product quality, less down-time of production lines and a reduced demand for the needed amount of lubricants during production, and the demand on hazardous lubricants can be strongly reduced. All in all this help at the same time to improve both the environment-friendliness and the cost-benefit ratio of production.

Introduction

When metal parts are formed or machined by tools and when wear parts are used, tribological problems will inevitably occur (tribology = the science of friction wear and lubrication). These are traditionally solved by using lubricants, which can be rather hazardous to the environment, or by using more expensive bulk material. In both cases this can mean that environmental issues are suffering.

Because of greater awareness of environmental issues and because of increased industrial competition with respect to productivity and product prices, new methods of surface treatment have been developed in recent years.

Some interesting points to be noted are that beside the direct environmental impact from using the processes (Midtgård 1993) there is also the influence that surface treatment of for instance tools can have on the use of tool materials, energy consumption in industrial production and last but not least, the reduced amounts of lubrication used and the possibility of using more environment-friendly lubricants, e.g. non-chlorided lubricants.

Technical description of processes

The processes to be discussed have quite a lot of similarities, and at the same time they are quite different. The processes will be presented in a natural sequence from the high temperature process of CVD through Plasma CVD, PVD and finally the very low temperature process of Ion Implantation. All the processes are very clean, but of course this does not mean that environmental problems do not attach to them.

CVD (Chemical Vapour Deposition)

In the mid 70's the standard (or Thermal) high temperature CVD process started gaining a market in Europe (Bryant 1977, Hintermann 1981, Bunshah et al. 1982). In this process certain volatile (gaseous) compounds are let into a vacuum chamber. The parts to be coated are mounted on shelves in the chamber. During the process, the system is heated to around 1000 °C and the gaseous compounds start to decompose and/or react chemically with each other, forming a surface coating on top of the parts in the chamber. Because of the high temperatures the coating does not just lie on top of the parts but diffuses into the material. This coating, therefore, has very good adhesion to the coated material. If the gases are equally distributed in the chamber all surfaces with the same temperature will get an equally thick coating. Since the gasses will disperse all over the chamber, all surfaces in holes and cavities will also be coated. The growth rate of the coatings will be around 0.1 - 5 μm/hour and a typical coating thickness is around 3 - 10 μm.

Typical CVD coatings are:

- TiC formed through the reaction:

$$TiCl_4 + CH_4 \rightarrow TiC + 4HCl$$

- TiN formed through the reaction:

$$2TiCl_4 + N_2 + 4H_2 \rightarrow 2TiN + 8HCl$$

It is also very simple to produce multilayers with a combination of these coatings. It is only a question of changing the gas mixtures during the process.

The main drawback of this process from a technical point of view is the high process temperature. Major efforts have been put into finding new process gases that can decompose and react at lower temperatures. Some progress has been obtained in this direction, but in all cases the new gases have been very hazardous to the environment, and today it seems that a different approach is preferred and well on its way to success. This process, Plasma Assisted CVD, is briefly discussed below.

PACVD (Plasma Assisted CVD)

PACVD is a new way of producing CVD coatings in an environment-friendly process with low process temperatures (< 500 °C), (Bunshah et al. 1982, Ojha 1982, Michalski et al. 1985). The PACVD process is very similar to standard CVD processes, but the parts to be coated need only be heated to around 500 °C. The coatings produced are the same as mentioned above under standard (thermal) CVD. The only major difference is that energy for decomposing the gases is put directly into the gas

via: DC pulsed currents, RF waves, micro waves or hot filaments. The process is still under development but its prospects look very promising indeed. And such equipment is already in use for production of wear coatings on tools. Typical coatings can be: TiN, TiC, TiCN, TiAlN.

The PACVD processes are also used to create Diamond or diamond like carbon (DLC) coatings from gas mixtures of Ar, CH_4 and C_2H_2.

With the plasma assisted processes (Plasma Assisted CVD or PVD (see below) it is furthermore possible to perform plasmanitriding either as the surface treatment itself or as a first surface treatment-step to be followed by a hard Plasma CVD or PVD coating. Coatings made with this double treatment is called "Duplex Coatings". They have shown very interesting potential. It is expected that duplex coating can become an interesting way of giving soft material (Aluminium etc.) a hard and wear resistant surface.

PVD (Physical Vapour Deposition)

PVD is a common denomination for several different but somewhat alike processes (Bhushan 1987, Esser et al. 1988, Leyendecker et al. 1991, Löffler 1993). In this process type, too, the parts to be coated are mounted on fixtures in a vacuum chamber. For PVD the fixtures have to be much more complicated than for CVD, because PVD is a so-called line-of-sight process, where only surfaces that "can be seen" are coated. It is, for example, only possible to coat sides in a hole to a depth equal to the diameter of the hole. It is therefore necessary to move and manipulate the parts during coating in order to ensure a proper and uniform coating.

Basically PVD coatings are formed in the following way. Target material (typically metal plates of Ti/TiAl/TiC/Cr) is evaporated in the chamber. The chamber atmosphere typically consists of N_2 and Ar. The evaporated material and the nitrogen in the chamber will form a plasma and the components will be drawn to the surfaces of the parts to be coated via a controlled voltage drop between the plasma and the parts. The evaporated material and ions from the gas will form a coating on top of the parts to be coated and on other surfaces in the chamber. The coating consists of: TiN, TiAlN, TiCN, or CrN depending on the target material. These coatings lie on top of the original material without the integration into the bulk material mentioned for CVD. The adhesion of PVD coatings can therefore often be a limiting factor when compared to CVD. Coating thicknesses for PVD coatings are typically 2 - 5 μm (an exception to this is CrN coatings which can be up to 15 - 20 μm thick).

PVD used for coating tools and wear parts and for decorative purposes can typically be divided into three main types:

A: Ion Plating, where the target material is evaporated via thermal heating (e.g. by bombardment with electrons),

B: Arc process, where the target material is evaporated by arcs,

C: (Unbalanced) Magnetron Sputtering, where the target material is evaporated via bombardment with Argon ions.

The three types produce similar coatings, but they have different effects on the working environment for personnel working with PVD coatings (see 'Environmental aspects of the processes themselves', below). Furthermore, the processes are typically performed at different temperatures:

A: 450 - 500 °C,

B: 350 - 450 °C

C: 300 - 350 °C

It is possible to produce PVD coatings at temperatures down to around 200 °C.

Ion Implantation

Ion Implantation is a process where ions created from gases, volatile chemical compounds or metal plates in a so-called ion source are accelerated to high speeds and bombarded into the surface of the material to be treated (Dearnaly et al. 1978, Straede 1992, Mikkelsen et al. 1992). Ion Implantation therefore does not create a coating but in reality it re-alloys the outermost layer ($< 0.5\ \mu m$) of the bulk material. Consequently, there is no risk of delamination, but the treated layer is very thin, and this can be a limiting factor when compared to PVD and CVD.

Ion Implantation is typically performed at temperatures below 200 - 250 °C and, in principle, it can be performed at room temperature.

In surface treatment of tools and wear parts the ions typically used are: N^+, Cr^+, C^+, Ti^+ and B^+.

- N^+ is formed from N_2 gas
- Cr^+ is now formed by sputtering from Chromium plates. Earlier on, it was formed from compounds of Chromium, Oxide and Chloride.
- C^+ is formed from CO_2. CO would probably give higher beam currents but has been discarded out of environmental considerations.
- Ti^+ is still formed from $TiCl_4$ but in the near future technical developments will make it possible to use sputtering from titanium plates instead.

- B^+ is formed by sputtering from boron containing metal plates. For environmental reasons this procedure is preferred to the use of BCl_3 or BF_3 known from the semiconductor industry.

Environmental aspects of the processes themselves

Before parts are treated with the above-mentioned processes they have to be carefully cleaned and degreased. Previously, this was done with very aggressive chemicals. Examples of materials used are: Trichlorine, ~~Fluor~~ Freon, Ethanol.

At the moment, a lot of effort is put into removing this type of chemicals from the cleaning stages. It is no problem to do so for CVD, PACVD (Grün 1993) and Ion Implantation, but it is still difficult for some PVD processes to obtain good adhesion without the use of such chemicals for the precleaning. Today, however, equipment is available (for instance equipment of type C) with a built-in RF cleaning stage, where the parts pass the final cleaning stage in the process chamber just before the coating starts, making the use of aggressive chemicals superfluous. In this case the parts are cleaned by Argon ion bombardment.

So today it is possible sufficiently to clean parts for surface treatment by using only water, demineralised water and alkaline water solutions in a heated ultrasonic bath.

For the CVD and plasma CVD processes mentioned above the remaining environmental issue is a question of taking care of the surplus gases from the process and the waste product, HCl.

The exhaust gas from the chamber is normally led through a so-called scrubber containing Sodium-Oxide. This will react with the HCl and form H_2O and NaCl instead.

Of course, the pump oil will be contaminated with the waste gases and the HCl, and therefore care must be taken when removing the pump oil.

When running Ion Implantation with the typical ions mentioned above for surface treatment of tools and wear parts, the environmental issue is mainly a question of being aware of contamination problems when cleaning the ion source. The same problem occurs in the PVD and CVD processes in connection with cleaning the chamber walls of old coatings.

Another question is of course if there are potential environmental problems connected with production of the target material (metal plates) that are normally produced from powder metal. As for the CVD processes care should also be taken when cleaning the pumps on the ion implanter, especially the pump for the ion source. With respect to this, it is important to remember that the use of target/ion source material for the Ion

Implantation process is extremely limited and far below what is used for CVD and PVD processes.

For PVD processes it is the same situation as mentioned above for CVD and Ion Implantation but on top of that one has to be aware of a potential danger to the working environment from another source, i.e. micro dust particles.

Micro dust particles are typically produced by PVD process types A and B (Löffler 1993, Midtgård 1993), not by process type C. When running types A or B it is necessary to be aware of the risk of dust inhalation, and when cleaning the chamber with a vacuum cleaner it is necessary to use an industrial vacuum cleaner with a water tank in order to avoid the risk of a dust explosion.

It is a common thing for the discussed processes that they have a relatively high energy consumption (electricity and water).

However, it is a fact that the result of surface treating tools and wear parts with these processes yields so much improvement in performance and reduction in the use of environmentally hazardous lubrication that the energy balance and environmental impact taken together clearly speak in favour of using the processes. Below will be given some examples of improved performance gained by using the processes.

Improved performance of treated parts

Several examples of improved performance of surface treated tools have been described in detail in Straede 1992, Mikkelsen 1992, Leyendecker 1991, Esser 1988, Rosell 1993, Keller et. al. 1991, Gühring 1994 and only a small number of typical examples will be mentioned here.

By Ion Implanting punching tools for aluminium the well-known problem of adhesion of the aluminium to the tool could be removed. Without surface treatment it was not possible to work without large amounts of lubrication. After implantation, both the use of lubrication and the tendency to adhesion were strongly reduced.

Ion Implantation of a knife cutting aluminium resulted in a substantially reduced tendency to cold welding and a 10 times improvement of tool life.

In another example punching tools for treating aluminium were PVD coated with CrN and afterwards ion implanted. Both treatments in themselves would be able to improve the performance of the tools but in this case the combination of the treatments gave an extreme improvement in performance. Without surface treatment it was not possible to produce at all without lubrication. After treatment with the combined process it was possible to punch 4000 holes without lubrication before the tool had to be renovated.

Another example of improvements obtained by Ion Implantation is cutting knives for meat, rubber and paper, where typical life improvements compared to untreated tools are around 5 - times.

Moulds and inlets for plastic extrusion moulds that are subjected to abrasive wear and corrosion are important areas where both Ion Implantation and PVD are used very successfully. An example is a gate for an injection mould subjected to abrasive wear where the life was improved by a factor of 3.5 (from around 300,000 shots to more than 1,000,000 shots) before refurbishment was needed.

In another example an injection mould was subjected to corrosive wear in some localized spots because of attack from aggressive gases from the plastic. By implanting chromium into the critical and localized spots it was possible to improve tool life by a factor of 12 (12 times longer life). For companies running production in three shifts around the clock it is very important not to have to stop the production. The cost of an unintended production stop can be much more expensive than the price of a tool although tools can be quite expensive.

It is not uncommon that the gain of a company using surface treatment on such tool parts gain more than 20 times the price of the surface treatment.

PVD coatings are typically used on moulds to improve slippage to plastics, to reduce wear of metal parts moving against each other and to improve performance of all types of cutting and forming tools. Typical life improvements for such tools by PVD coatings are not less than a factor of 5 to 10, and very often they will allow production at a higher speed and yield higher productivity and better product quality.

In fact it was recently stated and argued for in (Munck 1994) by a tool manufacturer that even if uncoated cutting tools were free it is more expensive to use uncoated cutting tools than to pay for PVD coated cutting tools if the total production costs for a given product is considered. The argument for this is higher productivity, less machine down-time and better quality of product.

CVD and Plasma CVD coatings are typically used on all kinds of tools where the high process temperature (especially for thermal CVD) can be tolerated. Tool types that are typically treated with CVD are hard metal cutting tools, inserts and forming tools. It has recently been documented that Plasma CVD coatings have a relatively very low tendency to material pick-up. This gives less tool wear, less machine down-time, better product quality, and the amount of lubrication can be reduced.

Environmental impact of improved performance

As indicated above, a surface coating will generally allow higher productivity and less use of energy for the production of the same amount of parts.

The prolonged tool life will result in a reduction in used material for the production of new tools. Furthermore, it is important to notice that it has also been shown in real life that the surface treatment of tools performed by the processes discussed in this paper do not create alloying problems in connection with remelting of tool material since the coatings are very thin and since the coatings will disintegrate during melting. These surface treatments do therefore not influence the possibility of recycling tool material.

One very important parameter, which is gaining more and more awareness, is the use of lubricants in industrial production, and at the moment a lot of effort is put into producing surface coatings allowing a substantial reduction in use of lubrication. The possibility of producing the "environment tool" is a widely discussed topic (Gühring 1994).

It is a fact that today it is already possible in a number of cases to reduce dramatically the use of lubricants when using coated tools. It is a hope for the future that today's chlorinated lubricants, which are necessary in highly demanding areas such as deep drawing of stainless steel, can be discarded (Keller 1991).

With a coating like TiAlN it is possible in several cases to cut steel without the use of lubricants. It is an area that still is under development. The TiAlN coating automatically forms an Al_2O_3 coating at the surface because of oxidation of some of the aluminium in the coating. The oxidized layer is a good thermal insulator and withstands high temperatures. It therefore takes care that the heat created during for example cutting of steel is dissipated through the removed material and not through the tool. If the heat were to be dissipated through the tool, the tool would be overheated and fail. For the production of a typical part the cost of lubrication used during production would be around 16% of the total cost of the part. The tool cost for producing the part would be around 4%. It is therefore clear that there will be a clear economic as well as environmental interest in becoming able to remove, or at least partly remove, lubrication. It will probably never be possible completely to get rid of lubrication in industrial production, but a strong reduction can be expected. It is also foreseeable that it will be more and more expensive to get rid of used lubrication because of increased environmental awareness.

Other examples of environmental gains from using plasma CVD, CVD or PVD is mentioned in (Grün 1993, Rosell 1993).

Summary

Summing up, there is no doubt that the above-mentioned processes can be used to decrease environmental problems in connection with industrial production. This does not mean that environmental dangers do not exist in connection with the processes. However, it does seem clear that it is possible to reduce the negative effects by choosing the environmentally milder versions of the processes and by general awareness of the potential negative effects. All in all there is no doubt that, taking an overall life cycle view, the use of these processes on tools and wear parts will have a positive effect on the environment.

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