Protective Coatings of Metal Surfaces by Cold Plasma Treatments

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October 1985
PROTECTIVE COATINGS OF METAL SURFACES
BY COLD PLASMA TREATMENT

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SUMMARY

The cold plasma techniques for deposition of various types of protective coatings are reviewed. The main advantage of these techniques for deposition of ceramic films is the lower process temperature, which enables heat treating of the metal prior to deposition. In the field of surface hardening of steel, significant reduction of treatment time and energy consumption were obtained. A simple model for the plasma - surface reactions in a cold plasma system is presented, and the plasma deposition techniques are discussed in view of this model.

INTRODUCTION

Cold plasmas are special from the scientific point of view, because they do not obey thermodynamical laws, and various species of different temperatures can co-exist in these plasmas without ever reaching thermodynamical equilibrium, not even on a local scale. Scientists define these plasmas as "non-LTE" i.e., without local thermodynamic equilibrium. Many species are encountered in these cold plasmas, like free electrons, ions (positive or negative), radicals, atoms and molecules. These constituents populations have different masses, different chemical affinities, different excitation states, and different temperatures. This latter characteristic is the reason for calling these plasmas non-LTE, because of the inequality in the temperatures of ions, electrons or radicals.

Thus, while the temperature of the neutral gas in such a plasma may reach a few hundred degrees, the temperature of the electrons may reach 50 000 K or more. It is this "chaos" that enables a very important use of the cold plasmas: reactions which require high temperatures and activation energies can occur while keeping substrates at low temperatures. The modern technology succeeded to exploit these advantages.

However, because of the very complex nature of the cold plasmas, our understanding of the processes occurring is much behind the technological

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applications in which such plasmas are being used. These applications include today fields like microelectronics (deposition and removal of thin and ultra thin layers), polymerization of plastics, ceramic coatings for wear and heat resistance, as well as surface treatments of steels and other metals. This paper will present a few of the used techniques, with an emphasis on metal finishing processes.

THEORY: REACTIONS IN GLOW DISCHARGES AND THEIR ATTRACTIVITY FOR COATING TECHNIQUES

A glow discharge plasma can be defined as a region of relatively low pressure (usually up to 20 mbar) and low temperature gas in which a degree of ionization in a quasineutral state is sustained by the presence of energetic electrons. When an electric field is applied to an ionized gas, energy is transferred more rapidly to the electrons than to the ions. Furthermore, in an elastic collision between an electron and a heavy particle (atom, molecule or ion) the energy lost by the electron is proportional to the mass-ratio between the electron and the particle, and is very small, and thus the electrons can accumulate sufficient kinetic energy from the external field to produce excitation or ionization of the heavy particles during the collisions. The production of these excited species, and their interactions with surfaces and growing films cause chain reactions, which result in the desired deposition product. Poll et al. (ref. 1) proposed the following description of the homogeneous (gas-phase) and heterogeneous (plasma-surface) interactions:

\[
\begin{array}{c}
\text{Monomer} \\
\downarrow k_1 \\
\text{reactive reaction product} \\
\downarrow k_2 \\
\text{polymer} \\
\downarrow k_3 \\
\text{Nonreactive reaction product (deposited film)} \\
\downarrow k_4 \quad k_5 \\
\end{array}
\]

This model points out that there are several reaction paths which may lead to the same desired results, thus making the reaction product more available. All these reactions may occur also in the reverse direction, making our understanding of all the processes even more difficult. According to the values of the kinetic constants \( k_1 \) for the forward and reverse reactions recombination may occur with increasing pressures or input power (ref. 2).

A typical arrangement for a cold plasma deposition system excited by a dc- or RF-discharge is shown in figure 1. The conditions required for obtaining a specific coating by the cold plasma technology have to be determined for a particular reactor configuration. These conditions include the optimal combination of pressure and power input for a set of specific gas feed composition and flow velocity.

In these processes the surface temperature is not important for the chemical reactions to occur. It affects however the composition and structure of the deposited product as well as the adhesion of the film to the substrate. In many cases where amorphicity is required, like in the production of amorphous silicon, the temperature should be low in order to avoid crystallization. On the other hand, if subsurface penetration of the deposited material is
Important, like in plasma carburization, the surface has to be heated to permit significant diffusion processes to occur (ref. 3).

In glow discharges therefore the substrate temperature can be controlled independently from the deposition and this is what makes these processes so attractive from the metallurgical point of view, as compared to other similar coating techniques, such as CVD. It has been shown for example by Inspektor et al. (ref. 4) that pyrolytic carbon plasma deposited at substrate temperatures of about 300 °C was of similar quality with pyrolitic graphite obtained at 1030 °C by CVD. Obviously, this characteristic of the cold plasma processes is very important for substrates which are to be kept at low temperatures for reasons such as preserving prior heat treatments, preventing undesirable phase transformations, undesired thermal gradients, etc. However, this is not the only advantage of this technique. It has been shown by various authors (refs. 5 and 6) that during plasma nitriding (a process also called ionitriding) the time of treatment is much shorter and the layer obtained is very homogeneous even for complicated parts' geometry, while the white compound layer can also be controlled by the process parameters. This effect of deeper and more homogeneous penetration has also been observed for plasma carburizing (ref. 3) and has been attributed to a higher rate of supply of C atoms to the surface of the austenite during the process. It should also be noted that the methane consumption in the plasma carburizing processes is much smaller as compared to conventional carburizing (ref. 3). These processes will be discussed in more detail in the forthcoming sections.

METALLURGICAL APPLICATIONS OF COLD PLASMA PROCESSES

Surface Hardening of Steels

The most known methods for hardening of low carbon steels are carburizing and nitriding. In recent years the carbon-nitriding process was developed (ref. 7), this process being simply a variation of carburizing in which some nitrogen is absorbed in austenite from ammonia added to the carburizing gas, in order to improve its hardenability by allowing oil quenching. Another additive used to improve hardenability in hypoeutectoid steel is boron. Steel boriding has become an effective means for wear protection and lately it has also been used for corrosion protection in acids and molten light metals (ref. 8). However, these processes usually require long treatment times. Conventional nitriding may require up to 50 hr at temperatures up to 592 °C, the Fe-N-eutectoid temperature. Carburizing is performed for many hours in a carbon atmosphere at ≈910 °C, and the boridation temperatures are also in the range of 900 °C.

The advantages which plasma processes may offer to these treatments are mainly (ref. 6): (a) reduced treatment times because of a more rapid saturation of the surface owing to the enhanced mass transfer through the plasma, (b) reduced gas consumption and (c) reduced energy consumption.

Nitriding and Carbonitriding

For these two processes the plasma technique has already become a well accepted industrial method. The suitable steels for these processes are the same as those for conventional nitriding. The best response to nitriding is
obtained when the steel contains Al, Cr, Ti, Mo, V or W, while unalloyed carbon steels tend to form an extremely brittle case. The alloyed steels are heat treated prior to nitriding. The plasma employed for these processes contains mainly nitrogen, with an addition of methane for carbonitriding (ref. 5), or an addition of hydrogen for improved properties (refs. 5, 6, and 9). It has been observed that the white layer can be controlled through the ratio between N₂ and H₂ in the gas feed. The N₂-H₂ mixture tends to favor the production of the γ'-Fe₄N layer. In the presence of methane in the plasma the layer ε-Fe₆₃₂-N is obtained. (This can also be ε'-Fe₃₂-NₓCᵧ) (refs. 5 and 6).

The efficiency of the nitride formation is directly correlated to the amount of N₂ in the gas feed, as indicated in figure 2, in which x-rays diffractograms of AISI M2 tool steel are presented for different nitriding plasmas. A detailed discussion of these diffractograms may be found elsewhere (ref. 9). However, it is interesting to note that the alloy richest in nitrides (fig. 2(c)) was not the one with the highest surface hardness. The highest hardness of VHN 1200 kg/mm² (~71 HRC) was observed for the M2 steels treated with a plasma mixture containing H₂:N₂ at a ratio of 1:1.

It is believed that the presence of hydrogen in the plasma improves the surface hardening by enhancing the solubility of nitrogen in iron. This is probably due to a lattice distortion caused by nitrogen and possibly hydrogen which increases internal stresses and hence the microhardness (ref. 9).

Carburizing

The main difference between carburizing and nitriding is that in the first the layer is obtained in the austenitic phase due to the poor solubility of carbon into ferrite. On a tonnage basis austenitic treatments enjoy a market some 900 percent greater than nitriding (ref. 6). However, to date there is no large-scale utilization of the plasma technique for these processes. This, in spite of the advantages mentioned above, and the very promising results obtained by Staines (ref. 10), Grube and Gay (refs. 3 and 11) and Jacobs and Metalsky (ref. 12). Staines (ref. 10) performed plasma carburizing of pure iron from a mixture of methane and hydrogen. Carbon profiles of samples treated for only 5 min at 1020 °C showed a substantial case with surface carbon levels in excess of 1 percent! After reheating and water quenching from 900 °C full martensitic hardness was obtained at the surface with a total case depth of 0.3 mm. In this case the samples were heated using the energy of the glow discharge only. Grube and Gay (refs. 3 and 11) however, have used auxiliary heating for the carburizing. They performed the carburization on AISI 1020 steel, using propane as the carbon gas at a pressure of 13 mbar. The plasma carburizing was performed for 10 min, but the heating was continued for 30 min to permit diffusion to take place. The results were compared to a vacuum carburizing process performed at a higher pressure (200 mbar) and for a longer time (32 min carburizing and 68 min diffusion times). The hardness obtained by plasma carburizing was higher than in alternative methods, including vacuum carburizing and values of 900 VHN were reached on the surface.

Recently, Jacobs and Metalsky (ref. 12) performed very accurate measurements of the carbon profiles carburized by different methods. They showed that the increase in the surface carbon level during plasma carburizing is so rapid that it is attained almost instantaneously. They also showed that for a good case depth and uniformity plasma cleaning should be applied. All these
results indicate that the basic advantages of the plasma processes are maintained for carburizing.

Boridation of steels differs from carburizing because there is no a priori requirement regarding the process temperatures. The conventional process is performed in the austenitic phase due to the higher diffusion at higher temperatures. However, even at high temperatures the solubility of B in austenite is not more than 0.005 percent. At 915 °C the boron solubility in austenite is 0.001 percent but in ferrite this solubility is practically zero (ref. 13). However, the fact that boron produces a surface compound and does not dissolve in Fe indicates the suitability of the cold plasma for the boridation of steel. It has been shown that boridation can be performed in cold plasma for substrate temperatures less than 600 °C (refs. 14 and 15). The steel samples for boridation were treated in plasmas of argon and boron gases such as diborane (B₂H₆) (ref. 18) or BCl₃ (ref. 15). Raveh et al. (ref. 15) added hydrogen to the plasma for the reduction of chlorine, while argon is used in such plasmas to enhance ionization and deposition rates (ref. 2). The microhardness of the samples reached about 900 VHN for B₂H₆ treated steels and about 1500 VHN for BCl₃ treated steels, as compared to the initial hardness of the samples - 270 kg/mm².

It appears that the borided layers contain the Fe-B and Fe₂B crystalline boride phases together with amorphous boron. A typical x-ray diffractogram of a plasma borided 4340 steel is shown in figure 3.

PROTECTIVE COATINGS FOR WEAR, HEAT, AND CORROSION RESISTANCE

Today's modern technology has high demands from the materials: improvement of lifetime of cutting tools, improvement of wear resistance, durability at high temperatures, etc. The answer to these requirements is usually given by ceramic coatings. Materials like hard nitrides and carbides of titanium, silicon, zirconium, hafnium and many others are used today for various applications. Nitrides are increasingly used in microelectronics and solar cells applications, as wear-reducing coatings for cutting tools and also as decorative coatings. Similar applications are encountered for carbides as well as for specific oxides. For corrosion protection plastic coatings are also applied (ref. 16). The specific ceramic layer for a certain use is matched to its substrate by taking into consideration their elastic moduli and Poisson ratio, their thermal expansion, the chemical adhesion etc. Sometimes when a specific coating like Al₂O₃ is required on a substrate like WC to which it has poor adhesion, an intermediate layer (TiC) is used to which both substrate and coating adhere much better (ref. 17). Thus, the required coatings and the problems involved have to be mastered prior to application. However, as far as the deposition itself is concerned, plasma techniques and CVD are the only methods which provide answers for direct thin film application, while CVD has the disadvantage of high temperatures, as mentioned. In this section we will present the most widely used cold plasma techniques for such coatings: P.V.D. and direct synthesis in plasma (electrodeless discharges). These processes permit, by correct design of the reactor and its components, to perform depositions of any desired film on any substrate, with good reproducibility and control of the process parameters.

P.V.D. - This general name comprises three basic processes: sputtering, evaporation and ion plating. The three processes require a solid metal source
as the starting material. A thorough review of these processes maybe found in reference 18.

Sputtering

A typical reactor used in this process is described in figure 4, with one electrode being the target and the part to be coated being the other electrode. In this setup an argon plasma is excited in the deposition chamber and the energetic argon ions sputter the material from the target and deposit it onto the workpiece. There are several combinations in which this method is being used. Usually, nitride and carbide films are obtained in this configuration by reactive sputtering. By introducing nitrogen or carbon-containing gases to the plasma, a chemical reaction is produced between the sputtered atoms of the target and the activated nitrogen or carbon species, producing the deposited coating. This is one very widely used method for producing TiN (ref. 19), as well as a broad range of other nitrides like HfN (ref. 20) or carbides (ref. 21).

A main advantage of the sputtering process is its versatility. A desired composition of the deposit can be achieved by co-sputtering, in which sputtering of several targets is performed in the same reactor and the composition of the deposits is proportional to the areas of the targets. This technique is widely used in microelectronics for preparation of stoichiometric intermetallic compounds like silicides (refs. 22 and 23). For specific purposes certain special geometries of electrodes have been developed, such as the hollow cathode for coating the outer surface of a wire (ref. 20). However, one disadvantage of the sputtering process is its low yield. As pointed out by Thorton (ref. 23) a typical yield (atoms sputtered per incident ion) for a 500 eV argon ion incident on a metal surface is 1, while during evaporation with the same energy 3 to 10 times more atoms can be evaporated.

Evaporation

In this method vapors are produced from a material located in a source which is heated by eddy currents, electron beam bombardment, laser beam or an electric discharge. The process is carried out at pressures like 10\(^{-5}\) torr, and the evaporated atoms undergo an essentially collisionless line-of-sight transport prior to condensation on the substrate. This is basically a vacuum deposition method where no plasma is employed. However a cold plasma can be activated during the process, thus obtaining the so-called activated reactive evaporation (ARE). TiN films were deposited by this method by evaporating titanium into a low voltage nitrogen plasma (ref. 24). The ARE method can be applied also for deposition of titanium carbonitride layers by adding carbon gases like C\(_2\)H\(_2\) to the nitrogen plasma (ref. 25). The layers such deposited reached Knoop hardness values up to 5900.

Ion Plating

In this process the material is vaporized in a method similar to that in the evaporation process, but the vapor flux passes through a glow discharge created by biasing the substrate to a high negative potential (-2 to -5 kV) and admitting a gas, usually argon, into the chamber at a pressure which may
reach 200 mtorr. Some of the vaporized atoms are ionized and are accelerated towards the substrate, creating a very adherent film because of the ion bombardment and the constant surface cleaning. The deposition rate however decreases (ref. 18) due to an inherent sputtering effect. By this method gold was deposited on nickel or iron substrates (ref. 26) for improved frictional properties, and TiN was also deposited by this method (ref. 27).

Direct Synthesis in Plasma (Electrodeless Discharges)

The characteristic of this important plasma technique is that no target or solid source is needed, and the desired deposit is obtained from direct reactions in the plasma. Thus, boron nitride (BN) coatings were deposited on steel from a mixture of BCl₃, NH₃ and argon (ref. 28), SiC was deposited on a titanium alloy from mixtures of tetramethylsilane (TMS), Ar and H₂ (ref. 29), Si₃N₄ from SiCl₄ or SiH₄ and NH₃ (refs. 30 and 31) etc. In all these cases inductively coupled RF plasma was utilized. Other types of coatings which were obtained by this technique are the pyrolytic graphite coatings obtained from methane or propane plasmas (ref. 4) or metallic titanium coatings on copper obtained from a plasma of TiCl₄ + H₂ + Ar (ref. 32). This type of plasma process is again one very widely used in microelectronics for deposition of photovoltaic films of amorphous or microcrystalline silicon (α-Si and μc-Si). Plasma deposition of such films has been performed by direct dissociation of SiH₄ (ref. 33), SiCl₄ (ref. 34), SiHCl₃ (ref. 35), and SiF₄ (ref. 36), as well as by sputtering from silicon targets (ref. 37).

A basic feature of these latter plasmas, which is not encountered in the P.V.D. processes is the polymerization. Any review of different coating processes would not be complete without mentioning the polymerized plastics for corrosion coatings. Schriber et al. (ref. 16) used a large volume microwave generator to coat steel substrates with organo-silicon films, and obtained a corrosion resistant coating which was tested for several weeks in a simulated marine environment without showing any traces of corrosion. By changing the deposition pressure and substrate temperature the organic nature of the film could be modified to inorganic (ref. 38).

CONCLUSIONS

The field of thin films deposition by plasma techniques is rapidly increasing and more methods and novel combinations of compounds are invented. It is beyond the scope of this limited review to scan all the possible techniques in this field. However, it should be emphasized that these techniques are possible due to the multiple homogeneous (gas phase) and heterogeneous (plasma-surface) interactions. From the materials point of view these techniques are sometimes more attractive than CVD due to the lower substrate temperatures.

These novel processes are most suitable especially in cases where earlier heat treatment of the substrate has to be preserved or where lower temperatures are imposed by the substrate material itself. Broadening of the applications of cold plasma techniques for coating processes is impeded by the lack of understanding of the effects the process parameters have on the deposition and on the properties of the coating. This will most probably be overcome in the future.
REFERENCES


Figure 1. - Schematic diagram of setup for plasma deposition of thin films.
Figure 2. - X-ray diffractograms of ion-nitrided AISI M2 tool steel samples obtained with copper radiation.
Figure 3. - X-ray diffractograms of 4340 steel sample borided at 500 W, 3 mbar for six hours, before and after the process.
Figure 4. - Schematic of planar diode sputtering system.
Abstract

The cold plasma techniques for deposition of various types of protective coatings are reviewed. The main advantage of these techniques for deposition of ceramic films is the lower process temperature, which enables heat treating of the metal prior to deposition. In the field of surface hardening of steel, significant reduction of treatment time and energy consumption were obtained. A simple model for the plasma - surface reactions in a cold plasma system is presented, and the plasma deposition techniques are discussed in view of this model.
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