Recent Developments in Corrosion/Erosion Control Using Refractory Materials Deposited by Radio Frequency Sputtering

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INTRODUCTION

In recent years the development of refractory materials has proceeded at a much faster rate than the ability of industry to utilize them effectively. This paper will discuss in detail some of the more interesting of these compounds, their potential for the petroleum industry and a process by which they may be uniformly applied to the surface of any object. Radio frequency sputtering is the name of the process and it is the intent of this paper to give sufficient detail as to the basic description and parameters of this process to enable the reader to implement it with a reasonable degree of effort. Results are cited that pertain to field problems.

THE SPUTTERING PHENOMENON

Although its extensive use is just now developing, sputtering was first reported in 1852 by Sir William Grove.[1] Sputtering is a process whereby gas ions in a vacuum system are accelerated by a high voltage to bombard a cathode (target) and cause ejection of atoms of cathode material. These high energy atoms immediately deposit on a nearby surface (substrate).

For many years sputtering has been known only for its adverse effects, such as forming conductive films and shorting out filaments in electron tubes. By the year 1930, approximately 190 papers had been written on sputtering and since then about 500 more. Only in the last decade have papers been published describing sputtering as a significant means of film deposition. This seemingly slow pace of utilization may be for the most part related to the development of a suitable state of the art of vacuum systems and related equipment essential for practical sputtering operations.

Since sputtering is a vacuum process, it becomes essential that some basic technology and terminology related to vacuum system operation be clearly understood. For example, Bernoulli's equation, so familiar to hydraulics, does not apply in high vacuum pumping. Bernoulli's term only applies in flow regimes where the mean free path between atomic collisions within the flowing fluid is of shorter length than the internal diameter of the vessel containing it. Table 1 gives some useful reference points and it is suggested that the reader not familiar with vacuum technology, pause long enough to acquaint himself with the physical concept of a system of 10 microns (10^{-2} torr) pressure before proceeding. This text will use the "torr" as the basic unit of pressure. Named after an early vacuum experimenter, Torricelli, this unit is now used instead of "millimeter of mercury". One atmosphere equals 760 torr. Since we are discussing thin film technology, it is worthwhile to develop a working concept of the angstrom unit (symbol Å) as a unit of length:

1 micron = 10^{-6} meters = 40 micro inches = 10,000Å

OR

1 Angstrom unit = 1/254,000,000 inch

Films referred to in this text will be in the order of 10,000 angstroms thick.

One of the most interesting facts to be observed in Table 1 is the large number of atomic collisions taking place at the various pressures. For example, there are 3.8×10^8 molecules striking a square centimeter of a surface at a pressure of 10^{-12} torr every second although at that pressure a gas molecule would travel roughly once around the earth before undergoing a collision with another gas molecule. This condition, where the mean free path between collisions is greater than the dimensions of the enclosing vessel, is known as "molecu-

TABLE 1

MOLECULAR INTERACTION AT VARIOUS PRESSURES

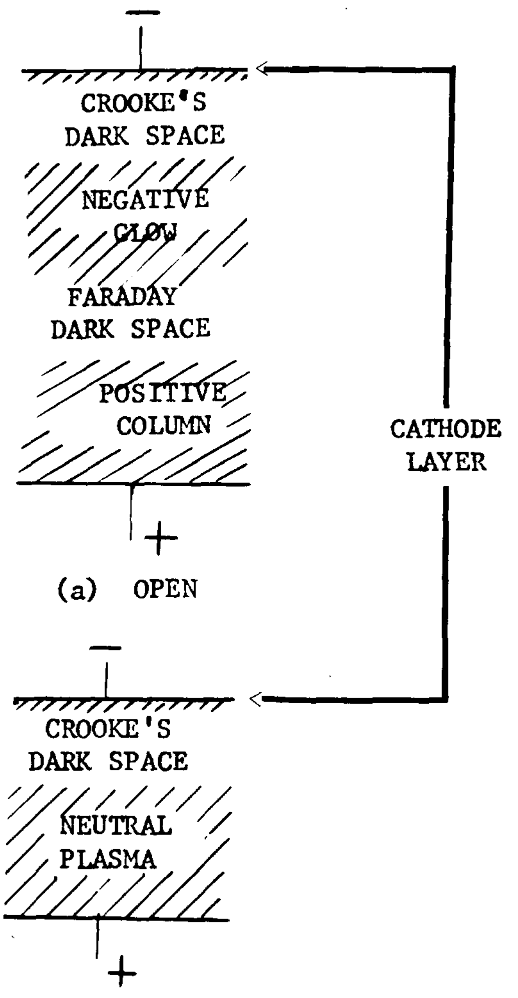
Pressure (torr)	760	.01	10^{-5}	10^{-12}
Collisions/Second	7×10^{9}	9×10^{4}	90	9×10^{-6}
Mean Free Path	6700Å	.5cm	5.1M	5.1×10^{4}KM
Molecules/CM^{2}/Sec Striking Surface	2.9×10^{23}	3.8×10^{18}	3.8×10^{15}	3.8×10^{8}
Monolayers/Sec Adhering to Clean Surface	3.8×10^{8}	4400	4.4	4×10^{-7}

lar flow" as opposed to the more normal "viscous flow" of classical fluid mechanics.

Plasma is the classic term for the fourth fundamental state of matter, i.e., a uniform mixture of positive ions and electrons.[2] A neutral plasma is used as a source for the positive ions that bombard a target during the sputtering process to liberate atoms of material for deposition. Thus the essential elements for a sputtering system are: (1) a vacuum system containing a sputtering cathode of desired material and configured to accommodate the desired substrates, (2) a source of electrical energy both to develop the initial glow discharge and to sustain the operation on a continuous basis, and (3) a controlled source of gas to maintain the right pressure despite a continual removal of gas from the system to assure purity.

It is important to understand how the glow discharge behaves, since it is the source of ions necessary to sustain the process. The principal regions in a low pressure glow discharge may be seen in Figure 1 (a). As the anode is physically moved closer to the cathode, both the positive column and the Faraday dark space will disappear with virtually no effect on the electrical characteristics of the glow. References 3 and 4 are excellent for those wishing a more detailed explanation of the physics of glow discharges. A glow typical of that in an operating sputtering system is shown in Figure 1 (b).

In the actual operation of the sputtering process, the voltage applied to the glow discharge is dropped across the Crooke's dark space.



(a) OPEN

(b) CLOSED

FIGURE 1
PRINCIPAL REGIONS
WITHIN A GLOW DISCHARGE

Ions move by diffusions through the neutral plasma. A positive ion reaching the surface of the plasma is attracted into the dark space and accelerated across it to collide with the target. At a constant temperature the thickness of the Crooke's dark space is inversely proportional to pressure. For argon plasmas the product of pressure and thickness is equal to approximately 0.3 torr-cm.[5] This constant relationship enables the operator to obtain a visual signal that relates directly to pressure during sputtering.

It is the high energy developed by the impinging ion as it accelerates across the space to strike the cathode that brings about a basic advantage of sputtering over conventional plating processes. As the ions strike the cathode, they cause atoms of target material to shoot back across the dark space where they in turn bombard the substrate. The particulate energy level in sputtering can easily be 1000 times greater than that exhibited by conventional plating processes and is sufficient to drive the atoms into the substrate atomic lattice. Also, since the atoms at typical sputtering pressures encounter about eight collisions in crossing the dark space, the process is capable of coating three-dimensional objects. This is not true for evaporative coating where a longer mean free path results in "shadowed" substrates.

The foregoing description of sputtering is valid for targets of any conductive material. For years this was a serious limitation, since some of the more desirable materials are insulators (AL_2O_3, SiO_2).

Anderson et. al. in 1962[6] show a method for deposition of sputtered insulator films. This is rf (radio frequency) sputtering and utilizes alternate ion and electron bombardment of the cathode surface to achieve deposition. When an rf signal is applied to a target electrode made of insulating material, a negative DC self-bias will develop on the surface of the target. This is essential for sputtering in that it gives a steady direction to the flow of positive ions across the dark space and may be explained in the following manner.

The charged particles present in the field are electrons and singly charged positive gas ions (usually argon). Particle mobility is a direct function of charge and varies inversely with mass. The mobility of the electron is approximately 10^5 greater than that of the ion. During the negative half cycle of the rf signal, more electrons than ions collect on the cathode surface and, since this surface is nonconductive, the electrons cannot leave on the positive half cycle. This has the effect of presenting a constant negative charge to the positive ions accelerating from the glow. Radio frequency sputtering is advantageous for metal sputtering as well, since there are many serious limitations to DC sputtering such as very low rates for refractory metals. To rf-sputter metals, requires, as with the insulator cathode, that a constant negative potential exist on the cathode. This is very simple to effect and requires only the insertion of an rf blocking capacitor in the power circuit.

Figure 2 shows a schematic of an operational sputtering system that can deposit either conductors or nonconductors. Traditionally, cleanliness in the system has been accomplished by the trapping of backstreaming contaminants from the oil diffusion pump by the use of liquid nitrogen. This has many disadvantages not the least of which are cost and inconvenience. The author has been successful in achieving trapping adequate for most industrial applications by using a thermoelectrically cooled baffle arrangement.

One of the most practical considerations for industrial sputtering is the deposition rate. This, in effect, determines the time required for a given coating. The system variables relate as follows:

$$\text{Rate} = f(NV/pd)$$

N is the number of ions present, V is the voltage drop across the dark space, p is the pressure and d is the target to substrate spacing. There are additional variables such as temperature and others specific to target material and gas mixture that will influence a specific deposition.

Mechanisms for handling large numbers of parts per cycle have now been developed and, with good technique, sputtered films can be produced to be price-competitive with conventional coatings. Equipment for sputtering, though presently effective, is extremely expensive and a thorough study of the references is recommended prior to implementing a sputtering operation.

In summary, rf sputtering offers the unique ability to deposit virtually any material onto anything else. Stoichiometry is preserved from the cathode to the deposited film. Sputtered films tend to be epitaxial; i.e., the surface topography is faithfully replicated. Hard films may be deposited with no need for subsequent grinding or polishing to restore a particular finish. Surface finish is not measurably changed during sputtering. With this deposition capability, the choice of materials for practical applications may now be considered.

MATERIAL SELECTION

By definition, a refractory material is distinguishable by its ability to resist heat. A ceramic is a material composed of a metal and another element, for example Al_2O_3. A cermet is a material composed of a ceramic phase and a metal phase, for example sintered tungsten carbide.[7] All three of the above terms are in common usage when extremely hard, temperature-resistant materials are discussed. It should be emphasized that rarely ever is one property alone sufficient to recommend a material for a given job. Sometimes variations can be surprising. If, for example, thermal conductivity at high temperature is desirable, silicon carbide conducts heat at 109 Btu/(hr,ft^2, °F/in.) at 2200°F. This is 70 percent of the value for chrome in nickel steels and 11 times the conduction of fire clay. Zirconia materials, on the other hand, are excellent insulators with a thermal conductivity about one-half that of fire clay brick although the bulk density of Zirconia is twice that of fire clay.

Chemical stability and erosion control seem to go hand-in-hand in petroleum industry applications. Well fluids and refinery processes involve some extremely corrosive agents, in many cases at high pressures and flow rates and with entrained particles of erosive material. Idealized oil industry coatings should be chosen not for one or the other but for a combination of corrosion and erosion resistant properties and perhaps other properties as well. The effect of friction is normally adverse, in which case a low coefficient is desirable. A low coefficient of friction coating can have the desirable effect of reducing surface temperatures, hence reducing corrosion. Table 2 gives some of the more interesting materials along with some comparative values. Complete information about these compounds, many of which are still in the laboratory, is not available at present.

Most "carbide" tools or inserts in use today are in reality cermets although metal carbide names are erroneously used to identify them. The major differences among cermets are those relating to the bonding between the ceramic and metal phases. Therefore, one should not be misled by attributing the above listed values, particularly chemical resistance, to a particular manufacturer's metal carbide product. Using a sputter cathode of pure material, one can successfully coat with any of the compounds listed in Table 2.

Hafnium carbide is an extremely promising material. Unfortunately, little is known about its chemical activity, and reported hardness figures vary considerably among authors. This may be attributed to its scarcity in pure form. HfC has been investigated as a substitute for industrial diamonds.[8] Boron nitride offers great promise. In one of its crystalline forms, it is harder than diamond and surpasses it in heat resistance. BN is unaffected by temperature alone up to 1500°C (diamond reverts to graphite at 900 degrees).[9] Titanium nitride appears to offer excellent all-around properties, including reasonable ductility. By virtue of its extremely good wear resistance and low coefficient of friction, TiN has found wide application as a coating for metal cutting tools.

Where lubrication of parts by conventional means is not practical, sputtered dry lubricant films are worth considering. Molybdenum disulphide is a viscous, grease-like material with a melting point of 1185°C. Surfaces sputtered with MoS_2 attain lubricity in the outer atomic layers. Although greasy in appearance, such surfaces may be rubbed with a white cloth leaving no visible stain on the cloth.

Hardness values shown in Table 2 are for conventional bulk properties. Table 3, reproduced from page 144 of reference 10, shows sputtered SiO_2 to be twice as hard as bulk-fired SiO_2. Because of the high formation energies, it is believed that this to some as yet unknown degree is generally true of sputtered films. Therefore, all hardness values in Table 2 should be considered as lower limit values for sputtered films.

SOME INTERESTING RESULTS

A considerable amount of evaluation work is presently underway and results will be forthcoming. In one completed field test involving flowline pressure regulators on a lease in Kansas, results have been very promising. This test involved some line pressure regulators that were sputtered with sapphire. The fluids contained corrosive agents as well as entrained

TABLE 2

PROPERTIES OF SOME REFRACTORY MATERIALS

Material	Formula	Hardness (knoop)	Melting Point(°C)	Coef. of Friction on Steel	Solubility
Nickel	Ni	557	1453	3	Acids
Quartz	SiO_2	830	2015	.5	HF
Chromium	Cr	935	1857		H_2SO_4,HCl
Zirconia	ZrO_2	1160	2677		H_2SO_4,HF
Chromium Carbide	Cr_3C_2	1300	1890		
Beryllia	BeO	1250	2550		
Tungsten Carbide (cobalt alloy)	WC · Co	1400-1800	2695	.4	HNO_3, HF Aqua Regia
Titanium Nitride	TiN	1800	2930	.12	Hot aqua regia+HF
Tantalum Carbide	TaC	2000	3880		H_2SO_4, HF
Alumina (sapphire)	Al_2O_3	2100	2015	.15	Very slightly sol. in acids and alkalis
Titanium Carbide	TiC	2470	3160		Aqua Regia HNO_3
Silicon Carbide	SiC	2480	2700		KOH
Boron Carbide	B_4C	2750	2450		Fused alkali
Hafnium Carbide	HfC	3000+	3890		
Diamond	C	7000	3700	.1	
Boron Nitride	BN			.1	Slightly sol. in hot acids

TABLE 3
MICRO HARDNESS DATA

Glass (over thermal SiO_2)	Weight at which fracture takes place (g)
Fired GSC-1	70-80
Sputtered GSC-1	140-160
Sputtered Quartz	140-160

sand particles. Evaluation at the end of one year in service showed the parts to be still serviceable although the normal life of untreated parts in this application was about five weeks. One wireline service company reports favorably on the results of a recorder bellows sputtered with tantalum pentoxide. Ta_2O_5 is moderately hard but extremely corrosive resistant. Well conditions were: depth of 12,000 ft, 9000 psi recorder, 275°F, H_2S content

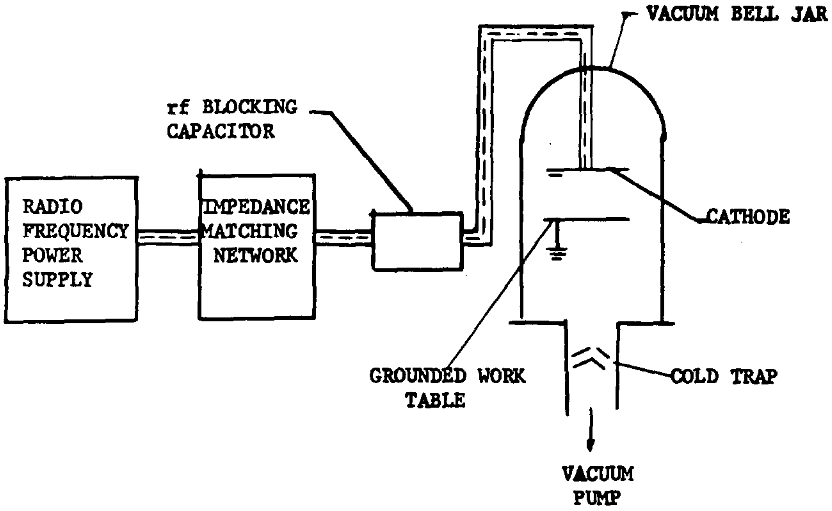


FIGURE 2

SCHEMATIC DIAGRAM OF rf SPUTTERING SYSTEM

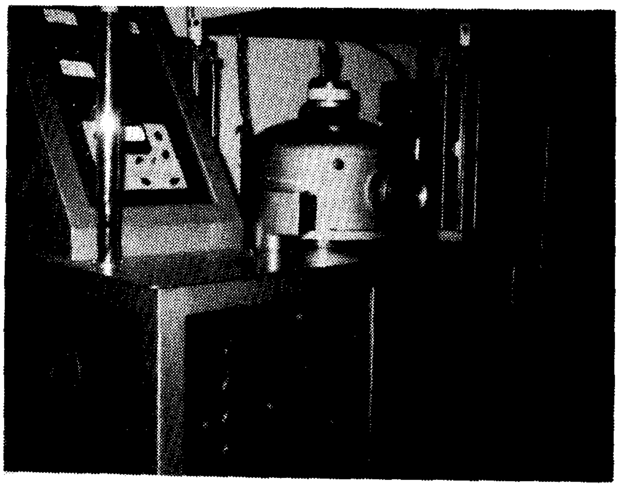


FIGURE 3

AN 8-KILOWATT rf SPUTTERING SYSTEM

(PHOTO COURTESY OF MEDITRONICS, INC.)

between 16 and 22 percent with a trace of CO_2. Results with laboratory specimens indicate that barrier films resistant to H_2S attack are readily obtainable by the rf sputtering process.

An excellent economic prospect is the application of sputtering to catalysts. For a few hundred dollars one can obtain a platinum cathode that would supply enough platinum to coat tons of alumina pellets with thin films of platinum.

CONCLUSIONS

Radio frequency sputtering has now arrived as a practical process for deposition of materials. Its universal deposition capability gives the designer a heretofore unavailable choice of materials for functional surfaces. Materials may now be selected for a combination of properties rather than those of a particular manufacturer. Application by this technique causes no measurable physical or metallurgical change in the substrate.

While the process is, by comparison, sophisticated, presently available systems make it cost-comparable to conventional electroplating.

Certainly it is difficult to imagine films of anything this thin being functional in oilfield applications. It should be remembered that typical thicknesses of all types of deposited films developed historically around optimum and economic values of the deposition process.

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