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SPUTTERING - A VACUUM DEPOSITION METHOD FOR COATING MATERIAL

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ABSTRACT

When sputtering is used to deposit coatings, practically any solid material can be sputter coated on any specimen regardless of its composition and geometrical complexity. Irregular surfaces can be coated into cavities and around corners when rf sputtering is used. The sputtering process is described in terms of its unique features: versatility, momentum transfer, configuration of target, precise controls and the relatively slow deposition rate. Sputtered films are evaluated in terms of adherence and coherence and internal stresses. The strong adherence is attributed to the high kinetic energies of the sputtered material, sputter etched (cleaned) surface and the submicroscopic particle size. A typical illustration is a sputtered solid film lubricant such as MoS_2. Friction tests were conducted on a thin, 2000 A° thick MoS_2 film. This film is superior to the thicker films applied by other methods. These films are very dense and without observable pinholes and the particle to particle cohesion is strong. Tolerances (film thickness) can be controlled to a millionth of a centimeter. Very adherent films of sputtered PTFE (teflon) can be deposited in a single operation on any type of material (metal, glass, paper) and on any geometrical configuration with a dense adherent film.

INTRODUCTION

Vacuum deposition methods can be divided into two categories: vapor deposition and plasma deposition methods. Vapor deposition can be described as thermal evaporation and condensation from a vapor phase to form a solid film. With plasma deposition methods direct current (dc) and radio frequency (rf) sputtering are performed in a plasma (ionized inert gas). Sputtering can be characterized where positive inert gas ions with high kinetic energies are accelerated toward the coating material (target). These ions have enough energy to overcome the binding energy of the target material and as a consequence lattice atoms are knocked out or sputtered. A substrate placed close to the target will intercept these sputtered particles and gradually build a film.

It is only recently that sputter-coating has become a serious competitor not only to the vapor deposition methods but also to the many other coating techniques. Sputtered films are already used very widely on commercial scale in the electronics industry where it is essential to the production of microminiature and integrated circuits. In addition to the electronic applications they are receiving an increasing level of acceptance in (1) the lubrication field to deposit solid film lubricants in order to reduce wear of sliding or rotating machinery components, (2) resistance to corrosion and oxidation, (3) for decorative purposes, (4) as coating for high reflectiveness, (5) coating razor blades for more corrosion, abrasion resistance and lubricating purposes, and (6) in many other countless applications.

The growing interest in sputtering originates from the fact that any solid material; conductors, semiconductors, insulators and even some organics can be deposited in the same composition as thin adherent films. These films can be deposited on specimens which can be composed of almost any material and be of very irregular geometry, and can be deposited to cover the entire surface. In many instances sputtering may be the only method which can be used when the requirements are to deposit high melting, multi-component complex materials in one operation. Typical examples are; (1) the deposition of stainless steel on plastics, or glass, (2) deposition of pyrex or quartz on metals, or (3) deposition of PTFE (teflon) on metals, glass, wood, and paper. The above three examples are just a few of the typical examples where sputtering is the only possible method of depositing the coating. These above films are deposited under accurately controlled experimental conditions with excellent reproducibility in film thickness and uniformity. Tolerances with sputtered films can be controlled to a millionth of a centimeter. One of the most important requirements of any coating regardless of its intended use is the adherence to the surface. The degree of adherence determines directly the usefulness and effectiveness of the coating. Sputtered films, have excellent adherence, when the correct materials selection is made.

The objectives of this paper are; (1) to describe the sputtering mechanisms and the unique features of the process, (2) the characteristics which can be expected from the sputtered films, and (3) finally give illustrations of sputtered films when exposed to severe mechanical testing (friction and tensile testing).

APPARATUS

Sputtering Modes

The simplest sputtering configuration, diode sputtering, consists of two electrodes, the coating material which is the target (cathode) and the specimen to be coated (anode). Both electrodes are located in a vacuum chamber which is first evacuated, then backfilled with inert gas, most commonly argon. A negative potential either through a dc (direct current) or rf (radio frequency) power supply is applied to the target. A voltage from 500 to 5000 volts between the cathode and anode is sufficient to ionize the gas and generate the plasma and induce sputtering. The positive argon ions from the plasma are accelerated toward the target with high kinetic energies, knocking off or sputtering atoms from the target surface.

Direct current sputtering is the oldest, simplest and also the least expensive method used. The limitatins to this method are that only conductors and selectively semiconductors can be sputtered. Nonconductors such as insulators (ceramics, glass, etc.) can not be sputtered by the dc method. The reason is that a positive charge accumulates on the targets' surface and from then on acts as a barrier to the impinging positive argon ions which prevents sputtering. This problem can be overcome by using an rf potential. Rf sputtering has the distinct advantage over the dc method that practically any solid, including insulators and organics, can be sputtered. In addition of sputtering insulators the sputtering process can be operated at significantly lower pressures (1 to 5 millitorr) and higher sputtering rates are obtained than with the dc potential. Due to these significant advantages, rf sputtering is the method of today and tomorrow, and therefore this discussion of sputtering will be devoted only to the rf method.

Radio Frequency Sputtering

In rf sputtering a high frequency potential in the low megacycle range is applied to the electrode which is water cooled, and onto which a circular target material is bonded. The rf current through the target injects power into the inert gas, thus generating the ion plasma by radio frequency fields. The present state of knowledge of rf sputtering has been described in detail (refs. 1 to 3). Figure 1 shows photographically the rf diode mode with the glow discharge during sputtering. When the specimen to be coated is placed in a close distance from the target about 3.2 centimeters and the argon pressure is maintained in the 2×10^{-2} torr range, complex geometrical specimens of any shape can be coated. Figure 2(a) illustrates the mounting of a seal 3.1 centimeters in height and 4 centimeters in diameter, to be coated. The inside and outside of the walls were coated and a possible flow of the sputtered material is shown in figure 2(b). The ion plasma which is generated by rf fields has apparently oscillatory effects on the sputtered material and also the backscattering effects contribute to the coating of irregularly shaped surfaces, thus going into cavities and around corners.

RF Sputtering with DC Bias

Today we have at least a dozen different sputtering arrangements and techniques utilizing additional electrodes in various combinations with rf and dc potentials. Figure 3 shows schematically a sputtering system which consists of two independently operated power supplies: rf sputtering and dc sputtering. The dc sputtering process is used strictly for cleaning or sputter etching of the specimen before rf sputter coating. The specimen is thus capable of sequential substrate cleaning or etching, followed by sputter coating or simultaneously etching (biasing) while sputter coating. Figure 4 shows photographically the complete sputtering assembly during sputtering. Using this assembly complex geometrical surfaces like ball bearings (fig. 5) can be coated without rotation, including the ball pockets.

DISCUSSION

Characteristics of Sputtering Process

Since sputtering is a plasma deposition method, there are a number of unique features which make it quite different from the other deposition methods. The principal advantages of sputtering from a production point of view are: (1) versatility, (2) momentum transfer, (3) reversibility, (4) configuration of source material, and (5) sputtering controls. Each of these features are briefly discussed below.

1. Versatility. Any solid material can be sputtered on practically any type of specimen. Alloys, intermetallics, inorganic compounds, glasses, ceramics, organics (very limited number have been sputtered). Organics such as teflon (PTFE) and polyimides have been successfully sputter-deposited. The specimen to be coated can be a material of any chemical composition: paper, plastics, glass, wood or metal.

2. Momentum transfer. The sputtered particles are transferred by a momentum transfer process as opposed to the thermal evaporation process. No direct heating is involved, therefore it is sometimes referred to as a "cold process". Since it is a nonevaporative process it does not depend on the vapor pressures of the constituent elements. The sputtered material arrives at the specimen with relatively high kinetic energies 15-60 ev (ref. 4).

3. Reversibility. Instead of applying a potential to the target, the potential can be first applied to the specimen to induce sputtering, this will sputter-etch or clean the specimen and is known as reverse sputtering. The purpose is to sputter etch or clean the surface of oxides and contaminants prior to applying a sputtered coating. This dual process - sputter etching and sputter coating results in a strong adherence of the film.

4. Configuration of source materials. Sputtering targets are usually area sources (instead of point sources like in evaporation) and the depositing atoms arrive from many different angles. Surfaces which are not in direct line of sight with the sputtering target, namely irregularly shaped surfaces can be coated in cavities and around corners without rotation in one operation.

5. Precise controls. Sputtering offers an extraordinary control over film thickness and uniformity. Tolerance requirements of a coating can be controlled to a millionth of a centimeter.

As any other deposition method, sputtering has one disadvantage, the deposition rates are relatively low. The average rate is 50 to 2000 A° per minute. The low depositon rates arise because when a surface is bombarded with ions, the major part of the energy really appears as heat in the target and only a small part goes into kinetic energy of the ejected atoms. To increase the sputtering rate, efficient ways must be found to cool the target. As a consequence, due to the low deposition rates sputtering is used where thin-films (in the micron range) are required. The low deposition rate has also certain advantages, it does afford a high degree of film control. The slow deposition rate (atom-by-atom) has a tendency to form dense films which are practically free of pinholes and the film approaches the theoretical density of the depositing material.

Characteristics of Sputtered Films

The usefulness of a coating, regardless of its intended use or application, depends on the degree of adherence. Adherence is directly related to surface pretreatment (cleanliness), energetics of the depositing material, type of interface formed and the selection of the film and substrate materials. When the features of the sputtering techniques are reviewed, the conditions are very favorable for strong adherence. The specimen surface can be conveniently cleaned from surface contaminants by sputter etching and immediately after the cleaning process the sputter-coating can be deposited. The sputtered atoms strike the surface with kinetic energies two or three orders of magnitude higher than thermally evaporated materials which have kinetic energy approximately 0.1 to 1 eV (ref. 5). The sputtered atoms due to the higher energy have a tendency to penetrate several atomic layers into the surface of the specimen. The strong adherence can be basically attributed to the surface cleanliness and the relatively high arrival energies of the sputtered material.

These energetic, submicroscopic sputtered particles have also certain activation energies which not only favorably affect surface adherence but also increase the cohesion between the sputtered particles. The strong particle to particle cohesion is responsible for the formation of high density films. Transmission electron micrographs have showed that these films are practically free of pinholes (ref. 6). This indicates that the density of these films is very close to the density of the bulk material. Formation of pinholes generally is interpreted as a result from poor adhesion. As a result of the strong adherence and coherence of these films, relatively thin films in the 2000 to 10 000 A° range can be used very successfully. It is well known that stress induced peeling which is caused by internal stresses in the film increases with film thickness. Therefore, sputtered films which are usually very thin (several microns), the stress induced peeling effect is substantially minimized. The thickness of the thin film can be very accurately controlled, thus practically elminating the possible tolerance requirements which are very significant when thicker films must be used. Due to these above characteristics of thin films, they are gradually starting to replace the thicker films applied by the other deposition methods.

The Utilization of Sputtered Films

Of the many possible applications where thin sputtered films have been used, one of the most distinct examples which illustrates the film functionability in respect to the film formation characteristics is in lubrication where sputtered solid films (MoS_2, WS_2, Au, Ag, etc.) are used as lubricants (ref. 7). MoS_2 for instance, can be sputtered stoichiometrically and its lubricating properties retained on sliding or rotating metal components which require lubrication. When solid film lubricants such as MoS_2 are sputtered on metal surfaces, only 2000 A° thick films are required for effective lubrication in vacuum or dry air (ref. 7). Low friction (f = 0.04) and extended wear lives are obtained as compared to the same films applied by other methods (fig. 6).

A comparison was made to evaluate the endurance lives during friction experiments on MoS_2 films applied by three different methods. Figure 6 shows graphically that the sputtered 2000 A° thick film exhibited the longest endurance life. The explanation of the long endurance life of the sputtered film is based on the strong adherence and coherence of the MoS_2 film.

MoS_2 films (2000 to 10 000 A°) were also sputtered on various tensile specimens (Ni, 440C, 52 000) and the film was evaluated during and after tensile testing (ref. 6). Figure 7 shows the tensile specimens before and after breaking. The surface topography of the elongated sections of the uncoated broken specimens is similar to the broken sections of the sputtered ones showing no scaling or peeling effects. The sputtered film on the broken sections of the specimen are intact, and the film plastically flows with the bulk material. The strong adherence again is explained in terms of the high arrival energies of the sputtered species and the minimized inherent stresses within the film due to its extreme thinness. These two severe mechanical tests (friction and tensile) performed on the sputtered films clearly demonstrate the excellent adherence and the desirable functional properties which thin films by sputtering can produce.

Another example which deserves comment is sputtered PTFE (teflon or polytetrafluoroethylene) films. PTFE has been successfully sputtered on metal, glass and paper surfaces. To discount the temperature effects during sputtering, PTFE was sputtered on a sheet of paper as shown in figure 8. The only observable change was the slight yellowish appearance of the sputtered film. The films were quantitatively analyzed for carbon and fluorine content (ref. 8). Adherence was exceptionally strong of the sputtered PTFE films on glass, metal, and paper surfaces. The film structure was qualitatively analyzed by electron transmission microscopy (ref. 8).

Sputter coating of PTFE introduces a direct method for the application of PTFE in a single operation to any surface. The PTFE coatings applied by previous methods had to be cured at elevated temperatures (about 680° F) and also required extensive surface preparation and primers to achieve good adhesion. The high curing temperatures eliminated many heat sensitive materials from the list of substrates that could be coated.

SUMMARY AND RESULTS

The sputtering method (rf) is discussed in terms of the unique features which sputtering offers in depositing coatings. The increased industrial applications of sputter-coatings originates from the fact that any solid material can be sputtered on almost any specimen regardless of its composition and geometrical complexity.

The sputtering process has unique features: versatility, momentum transfer, configuration of source materials, precise controls and the relatively low deposition rate. Sputtered films are evaluated in terms of adherence and coherence and the internal stresses. The strong adherence is explained on the basis of the high energy of the sputtered particles, the submicroscopic size and the sputter etched (cleaned) surface.

Distinct examples of sputtered MoS_2 illustrate the film functionability as a solid lubricant during friction and tensile tests. Sputtered MoS_2 films give longer endurance lives during friction experiments when compared to other deposition methods.

Conclusions are made that thin 2000 to 10 000 A° thick sputtered films are more effective than thicker films applied by other methods. Sputtered films are very dense and without observable pinholes. Tolerance requirements of sputtered films can be controlled to a millionth of a centimeter. Sputtering PTFE (teflon) introduces a simple method for applying adherent, thin teflon films at low temperatures to metal, glass and paper surfaces, in a single operation.

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RF SPUTTER COATING OF COMPLEX SPECIMENS

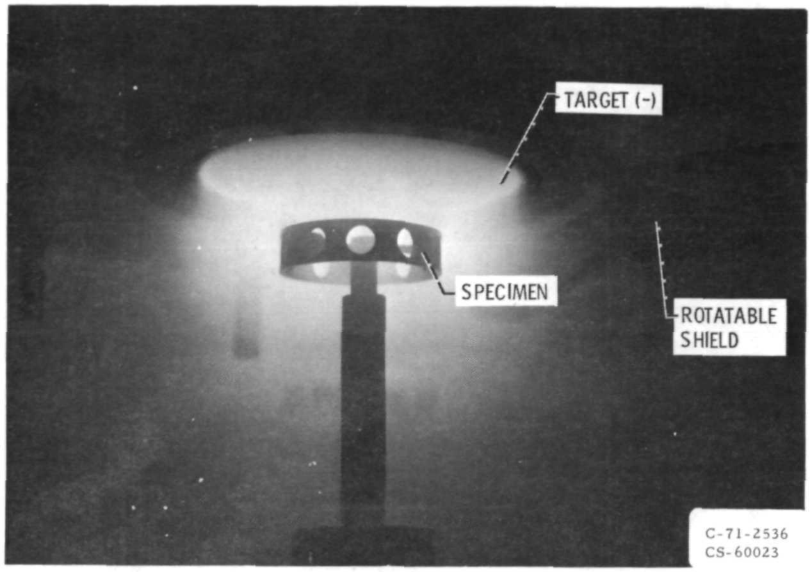
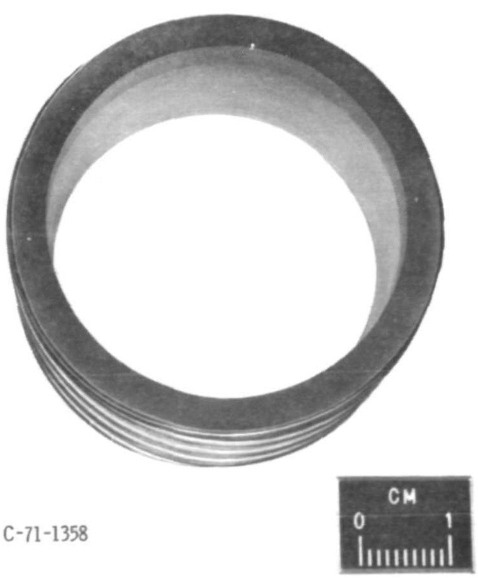


Fig. 1



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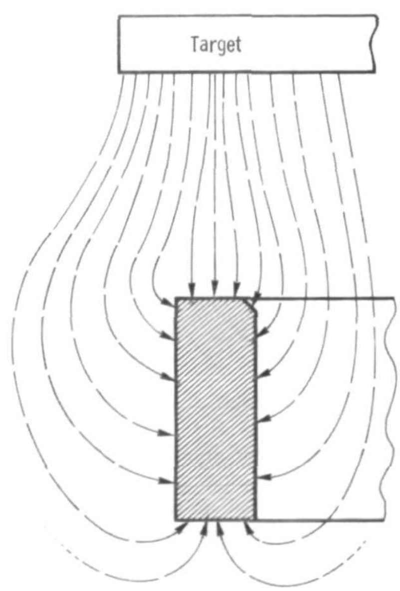

(a) Completely sputter coated seal specimen.

(b) Flow of sputtered material.

Figure 2. - Flow of rf-sputtered material to seal specimen.

RF WITH DC BIAS SPUTTERING SYSTEM

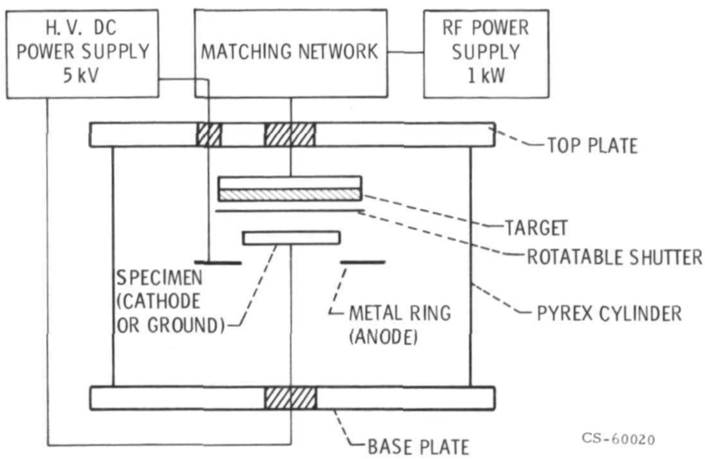

Fig. 3

RF WITH DC BIAS DURING SPUTTER COATING
OF COMPLEX SPECIMENS

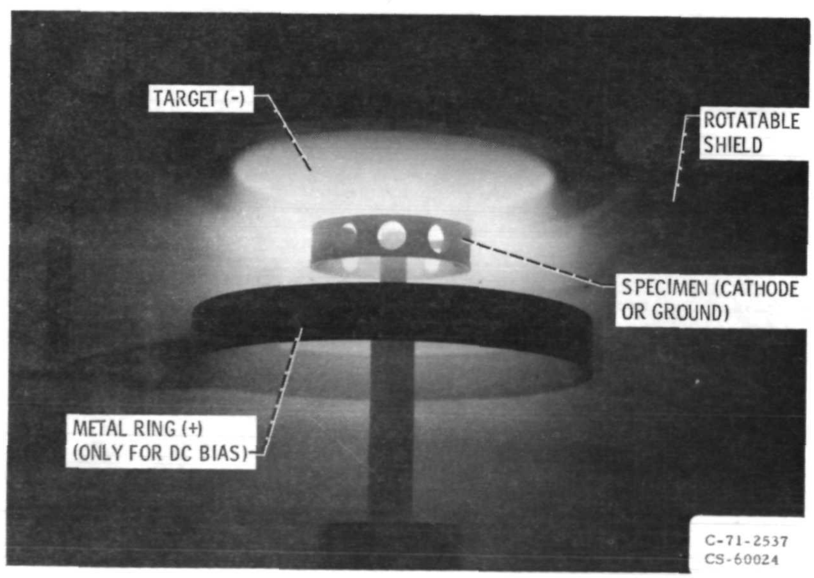

Fig. 4

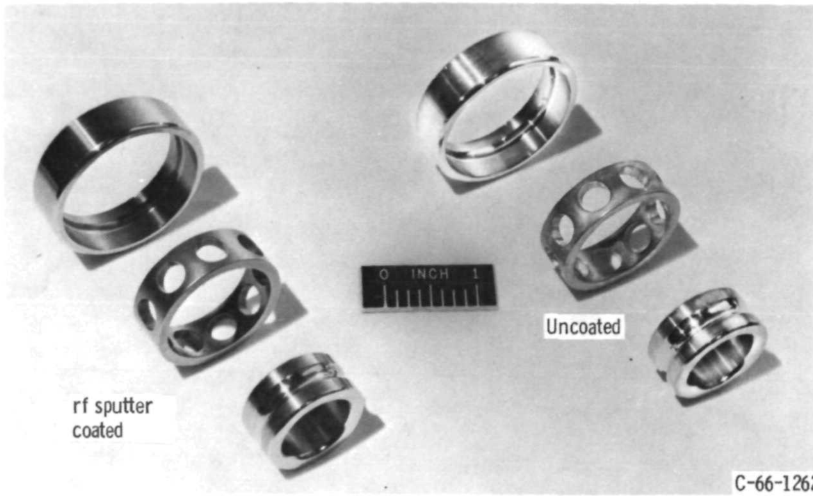

Figure5. - Ball bearing assembly completely coated with MoS_2 film by rf sputtering.

ENDURANCE LIVES OF MoS_2 FILMS APPLIED BY VARIOUS TECHNIQUES

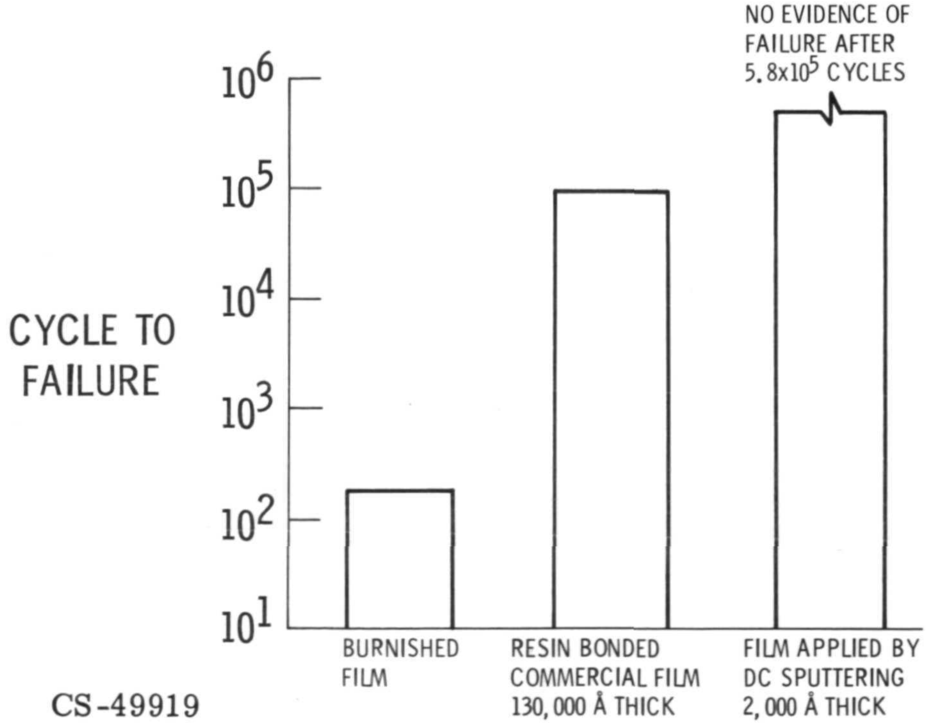

Fig. 6

COMPARISON OF UNCOATED AND RF SPUTTERED MoS_2 ON NICKEL AND INCONEL TENSILE SPECIMENS AFTER FRACTURE

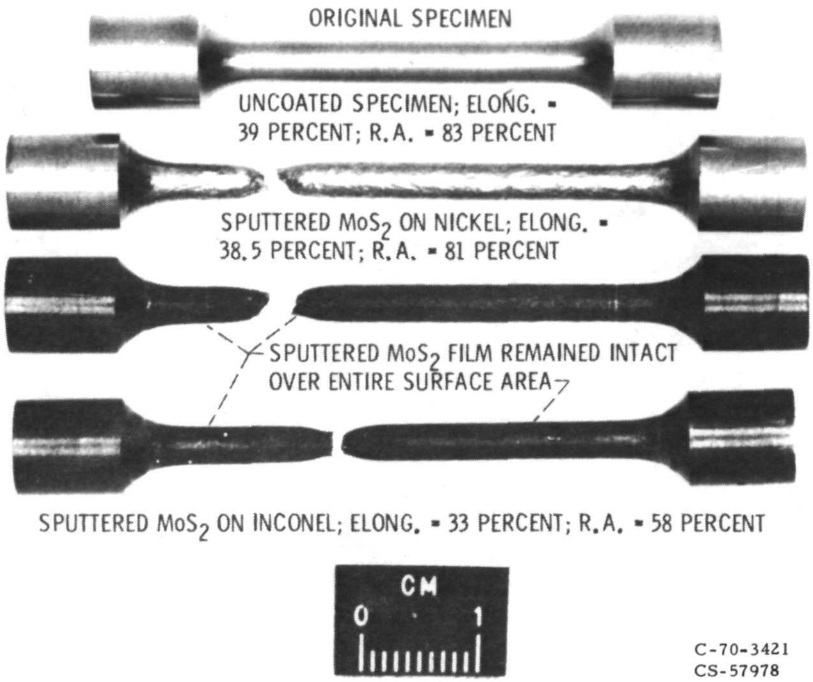

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Fig. 7

SPUTTERED PTFE ON PAPER

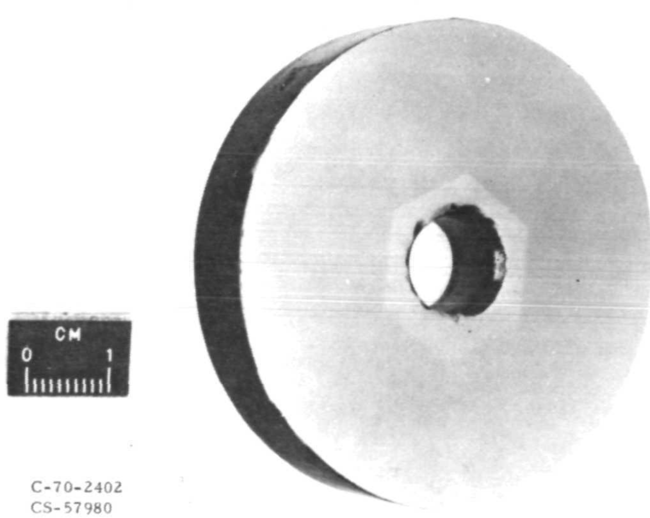

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Fig. 8