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Wakefield

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[54] **LOW TEMPERATURE METAL CARBONITRIDE COATINGS**

[75] Inventor: **Gene Felix Wakefield,** Richardson, Tex.

[73] Assignee: **Texas Instruments Incorporated,** Dallas, Tex.

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Related U.S. Application Data

[62] Division of Ser. No. 85,846, Nov. 2, 1970, abandoned.

[52] **U.S. Cl.** **29/195;** 204/192

[51] **Int. Cl.** **B32b 15/04**

[58] **Field of Search** ..... 29/195 A; 204/192

[56] **References Cited**

UNITED STATES PATENTS

3,466,156	9/1969	Peters et al.	29/195
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Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—E. L. Weise
Attorney, Agent, or Firm—Hal Levine; James T. Comfort; Gary C. Honeycutt

[57] **ABSTRACT**

Metal carbonitride coatings such as titanium carbonitride provide very hard, durable and abrasion-resistant coatings with low friction coefficients to the surfaces of various objects. For the temperature-sensitive objects such as those comprised of aluminum and glass, the metal carbonitride coating is produced upon the surface of a substrate by a vapor phase deposition process utilizing reactant compounds containing carbon, nitrogen and the metal. The surface of the object is cleaned, and the metal carbonitride is then bombarded with ions to sputter deposit it on the object at essentially room temperature, utilizing the coated substrate as the target.

3 Claims, 4 Drawing Figures

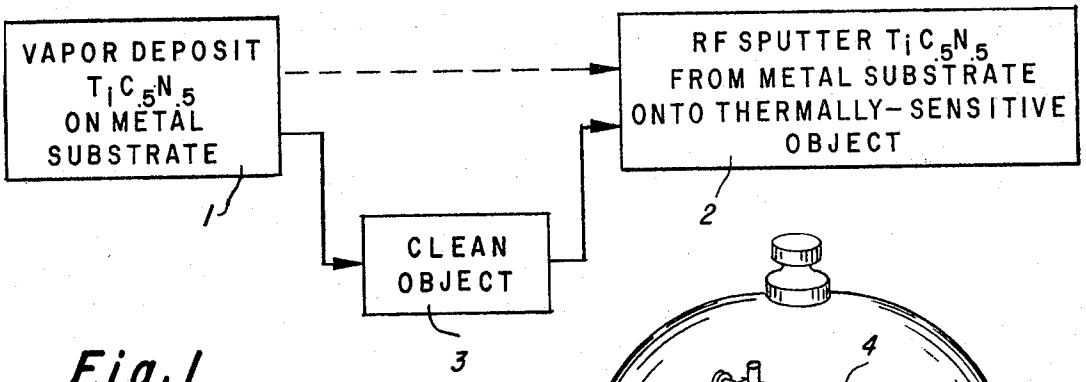


Fig. 1

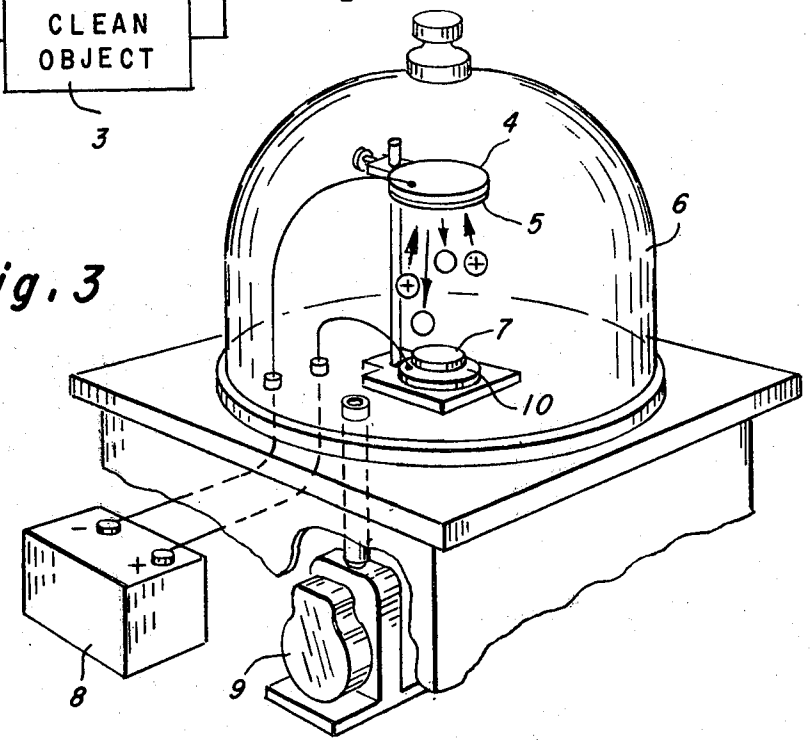


Fig. 3

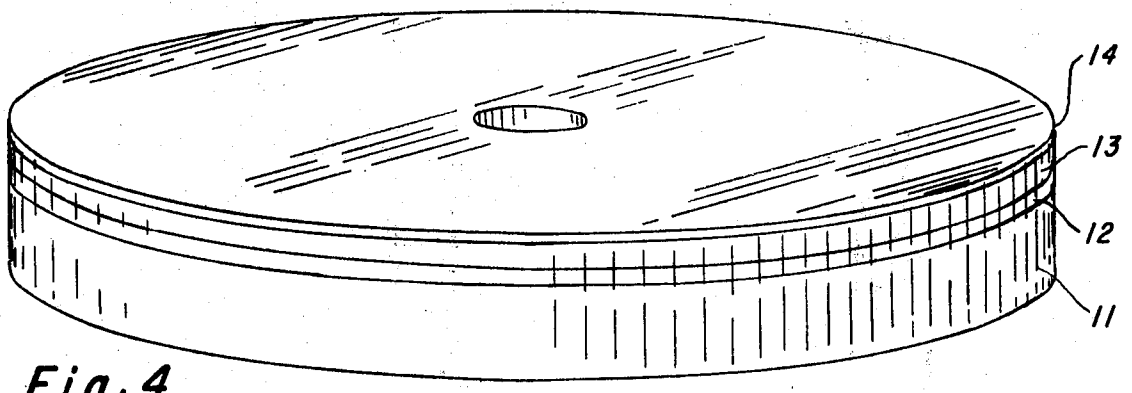


Fig. 4

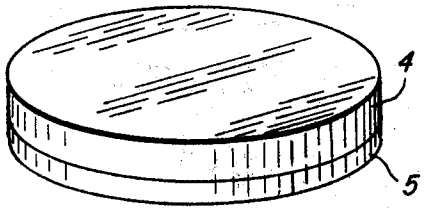


Fig. 2

INVENTOR
Gene Felix Wakefield

BY Gary C. Honeycutt
ATTORNEY

WITNESS Kathleen Sadacca

LOW TEMPERATURE METAL CARBONITRIDE COATINGS

This is a division of application Ser. No. 85,846, filed Nov. 2, 1970, now abandoned.

This invention relates to metal carbonitride coatings such as titanium carbonitride and, more particularly, to such metal carbonitride coatings applied to objects comprised of thermally sensitive material.

It has been found that metal carbonitride coatings such as titanium carbonitride provide very hard, durable and abrasion-resistant coatings on the surfaces of objects to which such coatings are applied. Until now, the metal carbonitride coatings have been produced directly upon the surface of the object to be coated by a vapor phase deposition process utilizing reactant compounds containing carbon, nitrogen and the metal. Such vapor deposition processes are described in copending patent applications Ser. Nos. 850,351, filed Aug. 15, 1969 now abandoned; 769,385, filed Oct. 21, **1968** now U.S. Pat. No. 3,846,162; 769,356, filed Oct. 21, 1968 now abandoned; and 769,372, filed Oct. 21, **1968,** now abandoned each assigned to the assignee of the present invention. The vapor deposition method of applying the metal carbonitride is not readily adaptable for coating objects which are destroyed at the temperatures at which the vapor deposition takes place, either because they have melting points lower than the temperature at which the substrate must be maintained during the vapor deposition or because the material which comprises the object to be coated will lose certain of its desired characteristics at such temperature. In particular, the vapor deposition process is usually required to take place at elevated temperatures of 700°C. and up. It would therefore be difficult to vapor deposit the metal carbonitride on aluminum which has a melting point of approximately 660°C., or glass which typically has a melting point of approximately 550°C. In addition, the grade of steel utilized for drill bits, taps, cutters and the like have a tendency to lose certain of their desirable mechanical properties when heated to temperatures of 700°C. and above, necessary for best results in the vapor deposition of the metal carbonitride.

In accordance with the present invention, the metal carbonitride can be deposited upon such temperature-sensitive objects at essentially room temperature. The metal carbonitride can therefore readily be applied to aluminum, glass, tool steel and other thermally sensitive materials, thereby improving the wear, friction, erosion, and/or galling resistance of the surfaces of such materials. In one embodiment, titanium carbonitride is coated on an adherent layer of magnetic memory film on an aluminum disk to provide a magnetic computer storage disk. The titanium carbonitride provides a wear-resistant surface for the storage disk and prevents damage by the occasional impact or contact of a read-write head with the disk. The process of the present invention is also particularly useful in the coating of razor blades, tools, bits, dyes, taps and many other objects where the material comprising the object is particularly sensitive to thermal treatment and the application of a thin coating to protect the surface will greatly improve the performance of the object.

It is therefore an object of the present invention to provide a method for coating thermally or temperature-sensitive objects such as those comprised of aluminum, glass, tool steel and the like with metal carbonitride coatings.

Another object of the invention is to provide a target or cathode comprised of a vapor-deposited layer of a composition on a metal substrate from which the composition may be sputtered, forming an adherent layer on other objects at low temperature and, in particular, where such compositions are metal carbonitrides.

A further object of the invention is to provide a wear-resistant coating for aluminum-comprising computer storage disks and drums and a process for manufacturing the same.

These and other objects are accomplished in accordance with the present invention by vapor-depositing a metal carbonitride such as titanium carbonitride ($TiC_{.5}N_{.5}$) on a metal substrate at a suitable temperature for the formation of such metal carbonitride. The object to be coated is then cleaned to assure good adherence of the coating to the object. The object is placed in a vacuum chamber sputtering apparatus and connected to the positive terminal of the power supply to act as the anode during the sputtering process. The metal substrate, which has been coated with the metal carbonitride during the vapor deposition process, is connected to the negative terminal of the power supply and acts as the cathode or target during the sputtering operations. The metal carbonitride is then bombarded with ions to sputter such material onto the cleaned object. For still better adherence, the polarity of the power supply is initially reversed, and some of the object material is first back sputtered.

In one embodiment of the invention, an aluminum-comprising computer storage disk or drum is made wear-resistant and resistant to damage by the occasional impact or contact of read-write heads by coating it with the metal carbonitride. The disk or drum is fabricated from aluminum to which adherent nickel layer is applied. Magnetic memory film is then adherently applied over the nickel layer by sputtering. Over the magnetic film titanium carbonitride or other metal carbonitride is applied by sputtering where the aluminum disk or drum with nickel and magnetic film layers becomes the object for the metal carbonitride coating.

Still further objects and advantages of the invention will be apparent from the following detailed description and claims and from the accompanying drawings illustrative of the invention wherein:

FIG. **1** is a flow diagram illustrating generally the process of the invention,

FIG. **2** illustrates the formation of a metal carbonitride cathode or target for the sputtering step of the invention,

FIG. **3** illustrates one apparatus utilized in the sputtering of the metal carbonitride on a temperature-sensitive object at essentially room temperature, and

FIG. **4** illustrates a computer storage disk fabricated in accordance with the present invention.

Referring then to the drawings, in simplest form, the process of the invention is as shown in FIG. **1.** Step **1** of the process is to vapor deposit the metal carbonitride on a metal substrate. The metal carbonitride is a solid solution carbonitride of a metal selected from silicon, boron, and transition metals in Groups IVB, VB and VIB of the Periodic Table, which in the present embodiment is titanium carbonitride ($TiC_{.5}N_{.5}$). This process includes the steps of heating the substrate to at least a decomposition temperature of the reactants

(generally about 700°C.) and then passing a gaseous stream containing the reactants over the substrate to thereby yield the reactants at the temperature of the substrate and permit the reaction of the metal, carbon and nitrogen, thereby forming a solid solution of the metal carbonitride on the metal substrate.

The reactants generally include a metal halide, e.g., titanium tetrachloride, molecular nitrogen and/or an easily decomposable nitrogencontaining compound, an easily decomposable carbon-containing compound (alternatively, an easily decomposable nitrogen and carbon-containing compound can be used), and molecular hydrogen as a reducing agent.

The metal carbonitride coating applied on the metal substrate by this vapor deposition method is a solid solution material having the metal, carbon and nitrogen within a single-phase crystal lattice. The vapor deposition step is described in copending patent application Ser. No. 769,356, referenced above. Other additions and improvements to the vapor deposition step are described in the other referenced copending applications.

Suitable metal-containing reacting compounds for the vapor deposition include metal halides. A preferred group of the metal halides is represented by the generic formula $Me(x)_n$ where n is a valence of Me, x is a halogen, e.g., fluorine, chlorine, bromine, and iodine, and Me is selected from silicon, boron, and transition metals as described above. Generally, the transition metal tetrahalides such as titanium tetrachloride are most preferred. However, the transition metal dihalides and trihalides are useful in some applications, particularly, higher-temperature coating operations. Suitable carbon-containing reacting compounds include cyclic and acyclic hydrocarbons having up to about eighteen carbon atoms which readily decompose at the deposition temperature. Examples of suitable hydrocarbons include the parafins such as methane, ethane, propane, butane, pentane, decane, pentadecane, octadecane and aromatics such as benzene and halogen-substituted derivatives thereof. Suitable reacting compounds containing both carbon and nitrogen include aminoalkanes, pyridines, hydrazines, and alkylamines. Some specific examples of reacting compounds containing both carbon and nitrogen include diaminethylene, triaminoethylene, pyridine, trimethylamine, triethylamine, hydrazine, methylhydrazine, and the like.

In one embodiment the vapor deposition coating process is conducted utilizing procedures and equipment whereby the metal substrate to be coated is maintained at the proper decomposition temperature (the temperature whereby the vaporous reactants decompose and form in the reactive state). Additionally, the vaporous reactant stream in the reaction zone around the metal substrate is maintained substantially below the decomposition temperature of the reacting compounds in a manner so that the unwanted products will not form in the vaporous state which are deleterious to the application of a smooth and continuous solid solution metal carbonitride coating on the metal substrate. The best results occur, with the reactants which decompose within the range of about 700°C. The preferred reactants include a titanium tetrahalide, e.g., titanium tetrachloride, an amine, e.g., trimethylamine, hydrogen and nitrogen.

Metal substrate **4**, illustrated in FIG. **2**, preferably consists essentially of molybdenum or copper. Coating **5** of the metal carbonitride is formed during the vapor deposition step to a thickness of 2 – 5 mils. The metal substrate in the present embodiment is approximately 5 inches in diameter and when coated, forms a 5 inch-diameter target or cathode for the sputtering step of the process.

Referring again to FIG. **1**, step **2** of the process of the invention is to sputter the metal carbonitride from the coating on the metal substrate onto the thermally sensitive object at essentially room temperature (ordinarily 18° – 27°C.). One apparatus which can be used to accomplish the sputtering operation is illustrated in FIG. **3**. The apparatus is comprised of vacuum chamber **6** and power supply **8**. Power supply **8** is preferably D.C. power supply upon which a radio frequency signal is imposed and should be set to approximately 800 watts for a 5 inch-diameter target. The target which consists of metal substrate **4** with adherent layer **5** of the metal carbonitride is connected to the negative polarity terminal of power supply **8** and thereby becomes the cathode for the sputtering operation. Thermally sensitive object **7** is placed on conductive pad **10** which is connected to the positive terminal and thereby becomes the anode for the sputtering operation.

Vacuum chamber **6** is filled with a nitrogen atmosphere for reactive sputtering and, with inert gases such as argon for non-reactive sputtering to provide ions. Pump **9** maintains a desired pressure in the vacuum chamber. The pressure is initially maintained at 50 milliTorr, as measured on a Pirani gauge, in order to start the glow discharge. Then, once the glow has started, the pressure is reduced to 6 milliTorr. The gas in the vacuum chamber is ionized, and the positive ions bombard the target. The metal carbonitride is thereby released from the target and a desired coating of from 2,000 – 3,000 angstroms of the metal carbonitride is deposited on the surface of object **7**.

It is essential when sputtering the metal carbonitride onto the temperature-sensitive object, that the material at the surface of the object be of pure virgin material in order to assure good adherence of the coating to the object. Cleaning step **3** intermediate steps **1** and **2**, as illustrated in FIG. **1**, is therefore inserted in a preferred embodiment of the process of the invention. Where the object is comprised of a ferrous material, such as a low carbon or tool steel, the cleaning process should include a first rinsing of the object with an organic solvent such as acetone to remove any grease from the surface. This should be followed by an acid etch in acids such as hydrochloric acid to remove any oxide from the surface. The object should then be rinsed in distilled water and dried with a clean nitrogen blast. After the object has been placed in the vacuum sputtering chamber, the polarity of the power supply should be reversed to back sputter and thereby remove any additional contaminating impurities from the surface of the object which might have adhered to the surface during the time between the cleaning process and the placement of the object in the vacuum chamber.

For aluminum, an etchant such as bright dip can be used to remove any oxide from the surface of the aluminum. Alternately, the aluminum may be highly polished by mechanical means to remove the oxide. Once the aluminum object has been placed in the vacuum chamber, the polarity of the power supply should be initially reversed to back sputter any additional impurities which might have contaminated the aluminum surface. If desired, a nickel preplate can be applied to the

aluminum following the bright dip or the mechanical polishing. The nickel is preplated by an electroless process such as dipping in a nickel solution. The back sputtering step should also be used after placing the nickel-plated aluminum object in the vacuum chamber.

Sulfuric acid and dichromate solution are utilized in cleaning the surface of a glass object. After the glass has been sufficiently cleaned, it is rinsed in distilled water and dried under a nitrogen blast. The back sputtering technique should also be used after placing the decontaminated glass object in the vacuum chamber.

The resulting metal carbonitride coating is very hard, durable, abrasion resistant and adherent. The friction coefficient is low, approximately 0.055 (few materials in solid solution contact have friction coefficients below 0.2).

Refractory metal coatings, other than metal carbonitrides, can also be formed by vapor deposition and then sputtered at room temperatures in accordance with the invention. For example, silicon carbide, boron carbide, titanium carbide, tungsten carbide, silicon nitride, titanium nitride and others are, in various embodiments, deposited in accordance with the invention.

In accordance with one embodiment of the invention, a metal carbonitride (preferably titanium carbonitride) is coated onto the surface of a magnetic storage disk or drum for a computer storage unit. The disk, illustrated in FIG. **4**, is fabricated as follows:

Nickel layer **12** is adherently formed on the surface of aluminum disk **11**. The size of aluminum disk **11** is determined by the requirements of the computer disk storage unit. Nickel layer **12** is formed to a thickness of approximately 2 mils and can be electrolessly plated onto the aluminum by dipping the disk in a nickel solution. Over the nickel layer, adherent layer **13** of magnetic memory film is applied by sputtering. Magnetic memory film layer **13** is comprised of a nickel-cobalt alloy having the required magnetic properties. Finally, aluminum disk **11** with nickel and magnetic film layers **12** and **13** is placed in the sputtering vacuum chamber in accordance with the above-described process, and titanium carbonitride protection layer **14** is applied to a thickness of between 2,000 and 3,000 angstroms. A light-weight computer storage disk is thereby provided having a surface which is scratch resistant, galling resistant and having low friction characteristics (the friction coefficient is approximately 0.055).

Although the process in accordance with the invention has been described specifically with respect to the coating of materials which have melting temperatures of less than 700°C., it will be noted that the process could be utilized with other materials having higher melting temperatures. For example, the process could be utilized with electronic components such as the silicon print head for a thermal printer (U.S. Pat. No. 3,496,333). particularly where thermally sensitive contacts have been placed on the silicon print head prior to the coating step.

Several embodiments of the invention have now been described in detail. It is to be noted, however, that these descriptions of specific embodiments are merely illustrative of the principles underlying the inventive concept. It is contemplated that various modifications of the disclosed embodiments, as well as other embodiments of the invention, will, without departing from the spirit and scope of the invention, be apparent to persons skilled in the art.

What is claimed is:

1. A computer storage disk or drum comprised of:

a. an aluminum substrate having at least one major surface,

b. an adherent nickel layer on said aluminum substrate,

c. an adherent magnetic film layer on said nickel layer, and

d. an adherent solid solution metal carbonitride coating on said magnetic film layer.

2. The structure of claim **1** wherein the metal carbonitride is titanium carbonitride.

3. The structure of claim **2** wherein the magnetic film is comprised of cobalt and nickel.

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