NASA/CR-97- 206059

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FINAL REPORT

TO

NASA MARSHALL SPACE FLIGHT CENTER

ON THE STUDY OF

LOW TEMPERATURE UNBALANCED MAGNETRON DEPOSITION OF HARD, WEAR-RESISTANT COATINGS FOR LIQUID-FILM BEARING APPLICATIONS

Contract Number NAG8-1020

January 15, 1996

by

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SUMMARY

The original program for evaluating the tribological properties several different hard coatings for liquid film bearing applications was curtailed when the time for the program was reduced from 3 years to 1. Of the several different coatings originally planned for evaluation, decided to concentrate on one coating, carbon nitride. At BIRL, we have been instrumental in the development of reactively sputtered carbon nitride coatings, and we have found that it is a very interesting new material with very good tribological properties. In this program, we found that the reactively sputtered carbon nitride does not bond well directly to hardened 440C stainless steel; but if an interlayer of titanium nitride is added between the carbon nitride and the 440C, the adhesion of the dual coating combination is very good. Statistically designed experiments were run with the dual layer combination, and 3 variables were chosen for the Box-Benken design, which were the titanium nitride interlayer thickness, the nitrogen partial pressure during the reactive sputtering of the carbon nitride, and the carbon nitride substrate bias voltage. Two responses were studied from these three variables were studied; the adhesion of the dual coating combination to the 440C substrate and the friction coefficient of the carbon nitride in dry sliding contact with 52100 steel in air. The best adhesion came with the thickness interlayer thickness studied, which was 4 μm, and the lowest coefficient of friction was 0.1, which was achieved when the bias voltage was in the range of -80 to - 120 V and the nitrogen partial pressure was 3 mTorr.

INTRODUCTION

BIRL, Northwestern University's industrial research laboratory, undertook a program for the National Aeronautics and Space Administration (NASA) to conduct unique and innovative research on the development of unbalanced magnetron sputtered coatings for improving the life of liquid-film bearings that are used in aerospace applications. Specifically, the objectives of the program were to:

- Determine the optimal process parameters to apply hard, wear-resistant, well-adhered coatings on materials for fluid film bearings such as 440C stainless steel or the Inconel 718 alloy without changing the metallurgical properties of those materials.

- Prepare friction and wear test samples with coatings of titanium nitride (TiN), molybdenum nitride (MoN_x), titanium aluminum nitride ($Ti_{0.5}Al_{0.5}N$), carbon nitride (CN_x), and polycrystalline superlattice titanium nitride/niobium nitride (TiN/NbN).

- Conduct friction and wear tests of the coated samples in tests that simulate conditions in fluid film bearings.

- Characterize and analyze the structure and properties of the coatings used in the friction and wear tests.

- Correlate the composition, properties, and performance of the coatings with the deposition conditions in order to determine the best coatings for friction and wear applications.

Soon after the program was started at BIRL, we learned that the funding had been reduced to 1 year from 3. To respond to this change, we scaled back our effort since it we would not be able to complete the full scope of work as originally intended. We decided to concentrate on one material that looked particularly promising, and that coating material was carbon nitride, CN_x. At BIRL, we have been instrumental in the development of CN_x, and we feel that it is a very promising tribological material with very interesting properties.

Carbon nitride was proposed by Liu and Cohen[1,2] to be a material that could theoretically be as hard as diamond if it could be synthesized in a structure analogous to β-Si_3N_4; i.e., β-C_3N_4. There has been a great deal of effort to try to synthesize crystalline β-C_3N_4, but to date it is doubtful that anyone has made a fully crystalline film of β-C_3N_4. Some people have claimed to have made the crystalline form, but upon closer evaluation the claims were not true. Usually what is deposited is a film with an amorphous matrix with possibly nanocrystalline areas in this amorphous matrix. The composition of the films has varied significantly with most of the films being significantly nitrogen deficient.

At BIRL, we have used the unbalanced magnetron sputtering process for the deposition of carbon nitride. Our films fit the description given above; i.e., they are amorphous and nitrogen deficient. They are CN_x, where x varies between 0.2 and 1.0 with typical values for x being between 0.2 and 0.4. It takes a special effort to increase the nitrogen content of the film above 0.4 to 1.0, and we have used an enhanced ionization technique[3] to increase the nitrogen content to where $x = 1.0$.

Even though we have not made the desired β-C_3N_4 coating, the material that we have deposited with a nitrogen content of $x = 0.2$-0.4 is very exciting. It is a hard material with a hardness of 15-25 GPa, but it is also very elastic, which is an unusual combination of properties. It is also a very interesting tribological material. Friction and wear tests have shown our carbon nitride coatings to have both low wear and low friction in sliding tests. Work by Li et al.[4] showed that CN_x films on zirconium substrates showed friction coefficients in the range of 0.1-0.2 against 52100 steel when run dry in air.

One area of concern with carbon nitride films is that the adhesion of the films to stainless steel has not been good. Work at BIRL in the early stages of this program that was discussed in our first report[5], showed that the adhesion of CN_x on stainless steel had a scratch test critical load of only 6-10 N for a 1 μm thick film, which is a relatively low value. A CN_x coating that failed in the scratch test at a load of 10 N is shown in Figure 1. TiN with a comparable thickness for example typically has a critical load of 20 N.

Fortunately, these adhesion problems can be overcome so that the excellent friction and wear properties of the carbon nitride can be utilized on a stainless steel substrate. Voevodin et al.[6] have shown that multilayer systems can produce the desired performance. Such multilayer

Figure 1. Scanning electron micrograph of the scratch track in a CN_x coating on 440C stainless steel substrate. The coating delaminated at a critical load of 10 N.

designs for tribological applications typically include a thin lubricating top layer and a hard load support layer as shown in Figures 2 and 3. However, in order to produce a successful coating/ substrate combination, attention has to be paid to the load support layer[7], which should be hard enough to prevent substrate deformation and resist abrasive wear. At the same time, this layer needs to be tough to prevent crack initiation and propagation as well as fatigue failure. And finally, the load support layer should adhere well to both the lubricating top layer and the substrate. Considering the above mentioned conditions, titanium nitride is an ideal candidate for a load support layer based on prior work done at BIRL.

Because of the potential interesting properties of carbon nitride for bearing applications and because of the reduced time frame to carry out our program, we decided to concentrate our efforts on the tribological characterization of carbon nitride produced by reactive unbalanced magnetron sputtering. The objectives for the program were thus revised, and for the 1 year effort the objectives were to:

- Tailor the reactive unbalanced magnetron sputtering process for depositing CN_x onto stainless steel substrates.

- Select an interlayer to enhance the adhesion of the CN_x coating and find the best deposition parameters that would give the highest scratch critical load value for the combined coating pair.

- Investigate the effect of deposition process parameters on the friction performance of the CN_x/TiN coating system.

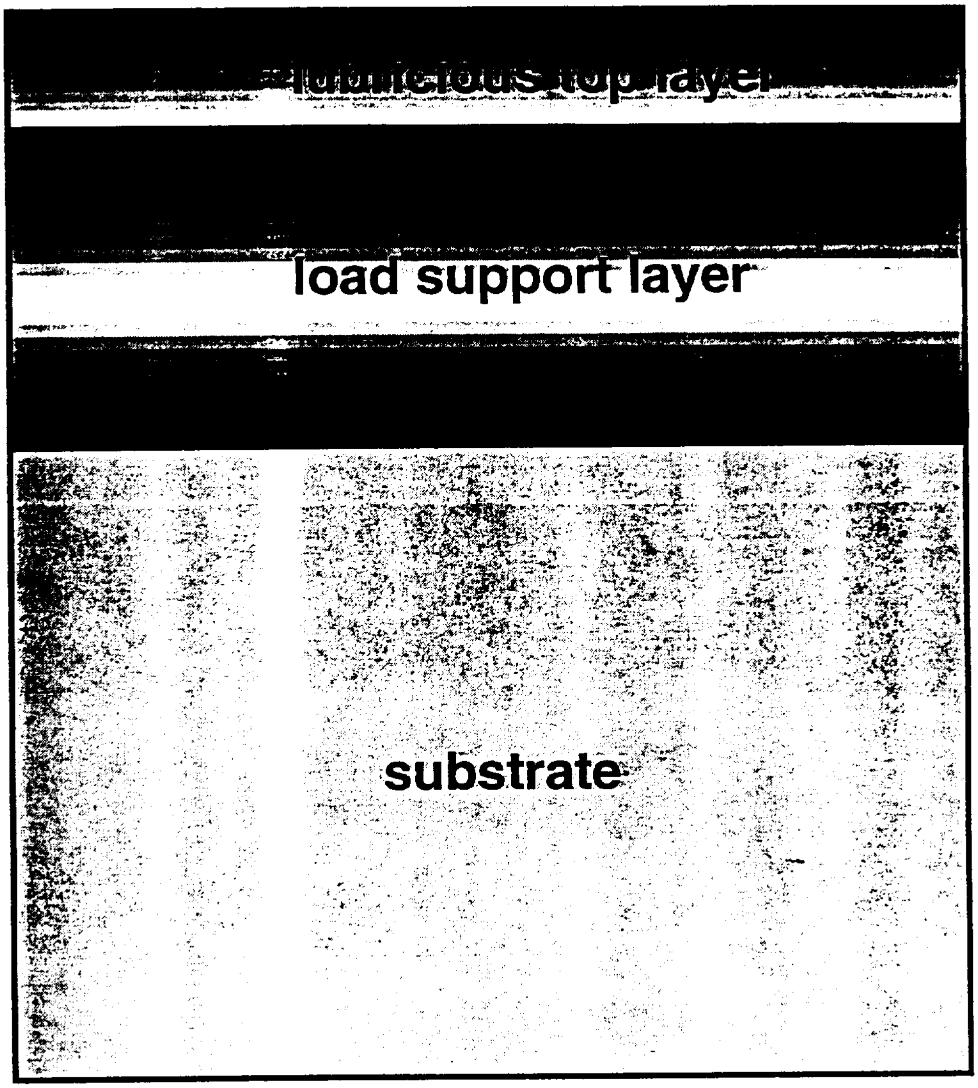

Figure 2. Schematic of the multilayer coating design for tribological applications.

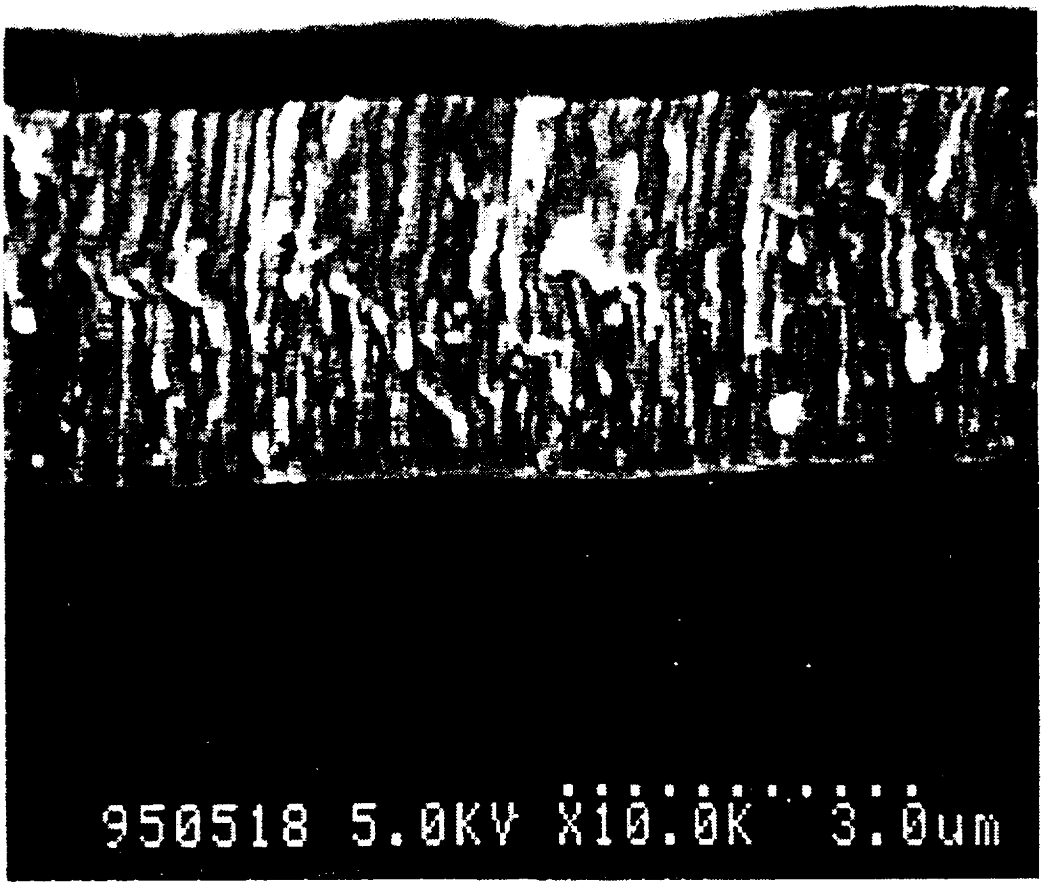

Figure 3. Cross section scanning electron micrograph of a typical CN_x/TiN dual coating on a silicon substrate.

EXPERIMENTAL CONDITIONS

Statistical Design

Statistically designed experiments were used to reduce the number of experiments required to investigate the influence of the process parameters on the coating-substrate performance. We used commercially available software called Design Expert[8] for the design of the experiments. A Box-Benken design[9] with a two level factorial design combined with incomplete block designs was employed for this research. This design offered desirable statistical properties, as well as a considerable smaller number of experiments than a full three level factorial design.

Reactive Sputter Deposition

Coating deposition was carried out in a Materials Research Corporation (MRC) 902M in-line sputtering system with two dc magnetrons, rf etching, and 30 kHz pulsed dc bias capabilities. The system is shown schematically in Figure 4. The target materials were titanium (99.94% pure) and graphite (99.9% pure). Nitrogen was introduced via a gas manifold around the magnetron edges, and the total system pressure was measured with a Baratron pressure transducer. The signal from the Baratron unit was fed back to the argon mass flow controller in order to maintain constant total system pressure during the operation of the coating unit. After ultrasonic cleaning in acetone and ethanol and drying in a nitrogen stream, the metallographically polished hardened (Rockwell C 59) 440C stainless steel substrates were placed on a stainless steel palette and introduced into the chamber via the load lock.

Sputter etching of the substrates began when a base pressure 1×10^{-6} Torr was reached. The substrates were etched for 5 minutes at a power level of 1.5 kW to the substrate pallet that had a surface area of approximately 930 cm^2. The TiN deposition was performed at 8 mTorr total pressure, 0.32 mTorr nitrogen partial pressure, and -100 V pulsed substrate bias potential. The

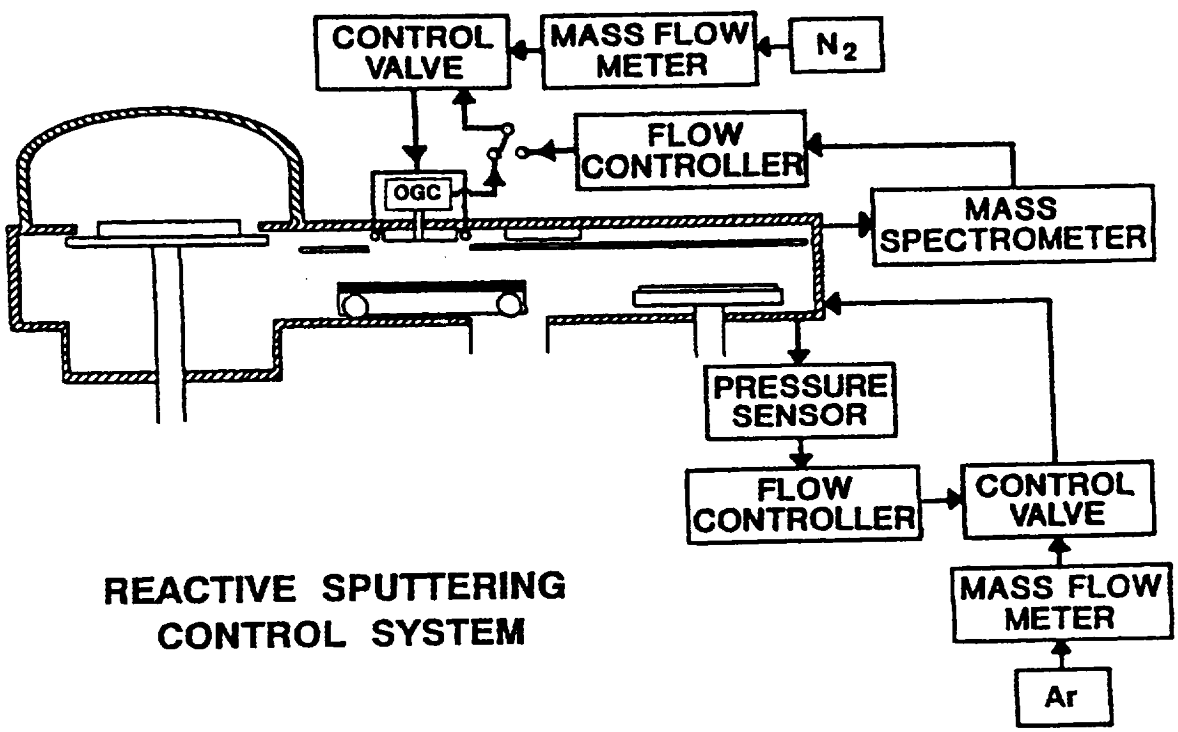

Figure 4. Schematic diagram of the Materials Research Corporation 902M in-line sputtering system that was used to reactively sputter deposit the TiN and CN_x coatings for this program.

nitrogen partial pressure during the deposition of the TiN, as measured by the mass spectrometer, was kept constant with an automatic closed feedback control loop.

From prior sputtering experiments, the substrate bias as well as the nitrogen partial pressure were known to have considerable influence on the properties of the deposited CN_x films[10]. The deposition of the CN_x coatings was done at significantly higher nitrogen partial pressures than the TiN coatings, and the nitrogen partial pressure during the deposition of CN_x was controlled with flow control rather than the customary partial pressure control due to the high nitrogen partial pressure. The nitrogen partial pressure was varied from 1-3 mTorr, and the total system pressure was 2-6 mTorr since the ratio of nitrogen to argon was always 1 to 1. This ratio was chosen based on the work of Li[10], who showed that reasonable deposition rates could be achieved under these conditions.

With the high nitrogen partial pressure during the deposition of CN_x, the graphite target was running in the so-called poisoned mode where the surface of the target was covered with a carbon-nitrogen compound. The substrate bias was varied from -50 to -400 V, and the thickness of the TiN support layer ranged between 0.001 to 4 µm. The deposition rate for each new condition was investigated prior to every experiment in order to achieve a constant CN_x top layer thickness of 1 µm. This CN_x thickness was found to be sufficient to give the desired tribological properties. The top layer of this dual layer coating defines the sliding properties of the system as long as it lasts, and the load support layer stabilizes the coating-substrate system in terms of loading.

Adhesion and Friction and Wear Tests

The adhesion of the coatings was measured with a CSEM manual scratch tester at load intervals of 200 g. The acoustical signal was used to determine the critical load. Post facto scanning electron microscopy was used to determine the failure mechanism.

A block-on-ring friction and wear test was used to investigate the friction coefficient. All tests were carried out in the ambient atmosphere with a relative humidity of 45% ± 5%. The load on the stainless steel ring was 100 g, resulting in a Hertzian pressure of 191 MPa. The sliding speed was 8.4 m/min, and the sliding distance was 100 m. The relative error of the friction coefficient was ±10% and was determined from control readings from a stainless steel sliding wear couple in lubricated contact prior to every measurement.

Data Treatment

The response surfaces were calculated on the basis of the Box-Benken design. Linear, quadratic, and cubic polynomials were fitted to the response. The quadratic model was chosen on the basis of the summary of analysis of variance (ANOVA)[8].

RESULTS AND DISCUSSION

Adhesion Response Surface

The adhesion response surfaces of the interlayer thickness, substrate bias voltage, and nitrogen partial pressure were investigated. Independent of all of the processing parameters, the CN_x failed every time at the CN_x/TiN interface. A failure at the TiN/stainless steel interface was never observed. Both the TiN interlayer thickness as well as the substrate bias voltage level for the deposition of the CN_x top layer were identified as parameters of major influence. The nitrogen partial pressure influenced adhesion very little over the pressure range studied of 1-3 mTorr.

Figures 5-7 show the three dimensional adhesion response surface of the substrate bias potential, the TiN interlayer thickness,and the nitrogen partial pressure. The maximum in adhesion is found for the 1 mTorr nitrogen partial pressure at a interlayer thickness of 4 µm and a substrate bias of -120 V. The most influential parameter for the adhesion is the TiN interlayer thickness.

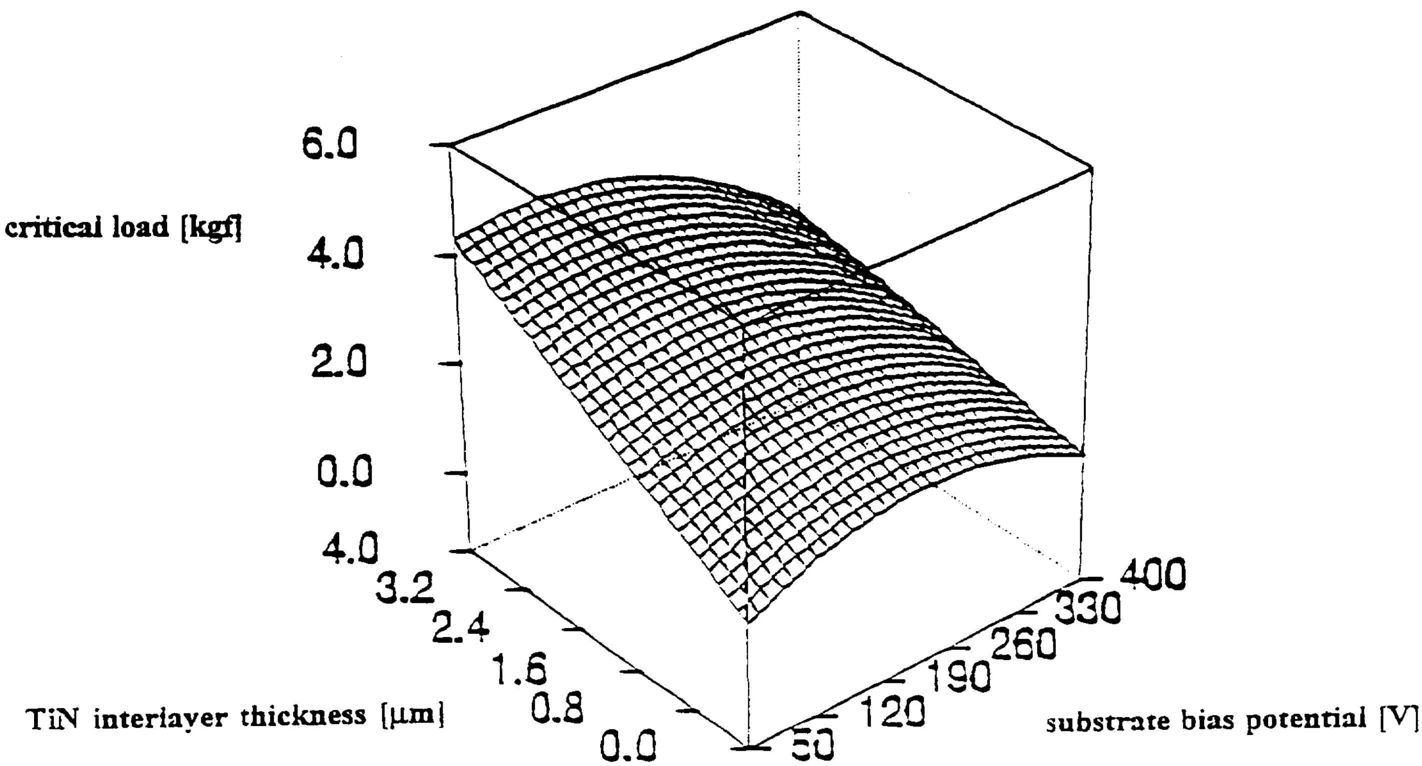

Figure 5. The three-dimensional adhesion response surface of the substrate bias potential and the TiN interlayer thickness at 1 mTorr nitrogen partial pressure.

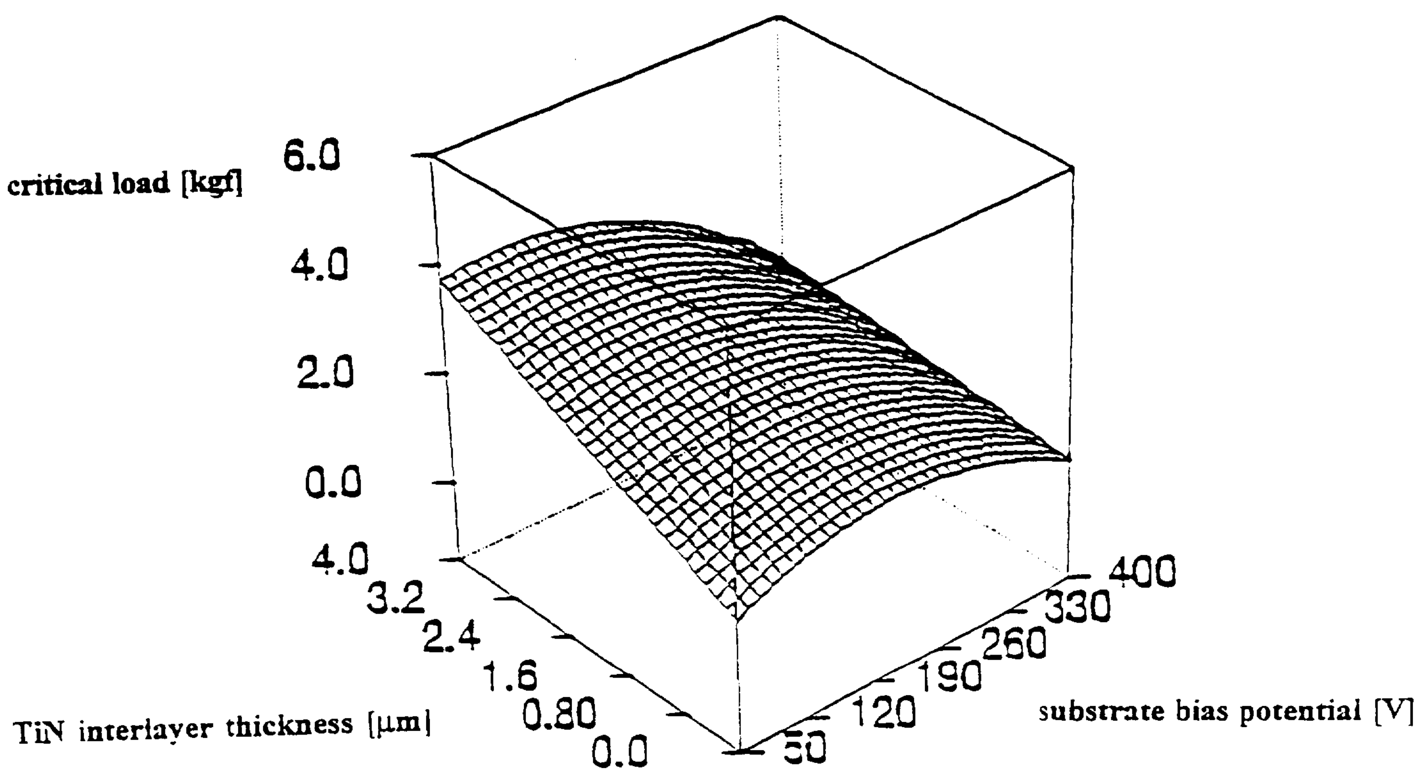

Figure 6. The three-dimensional adhesion response surface of the substrate bias potential and the TiN interlayer thickness at 2 mTorr nitrogen partial pressure.

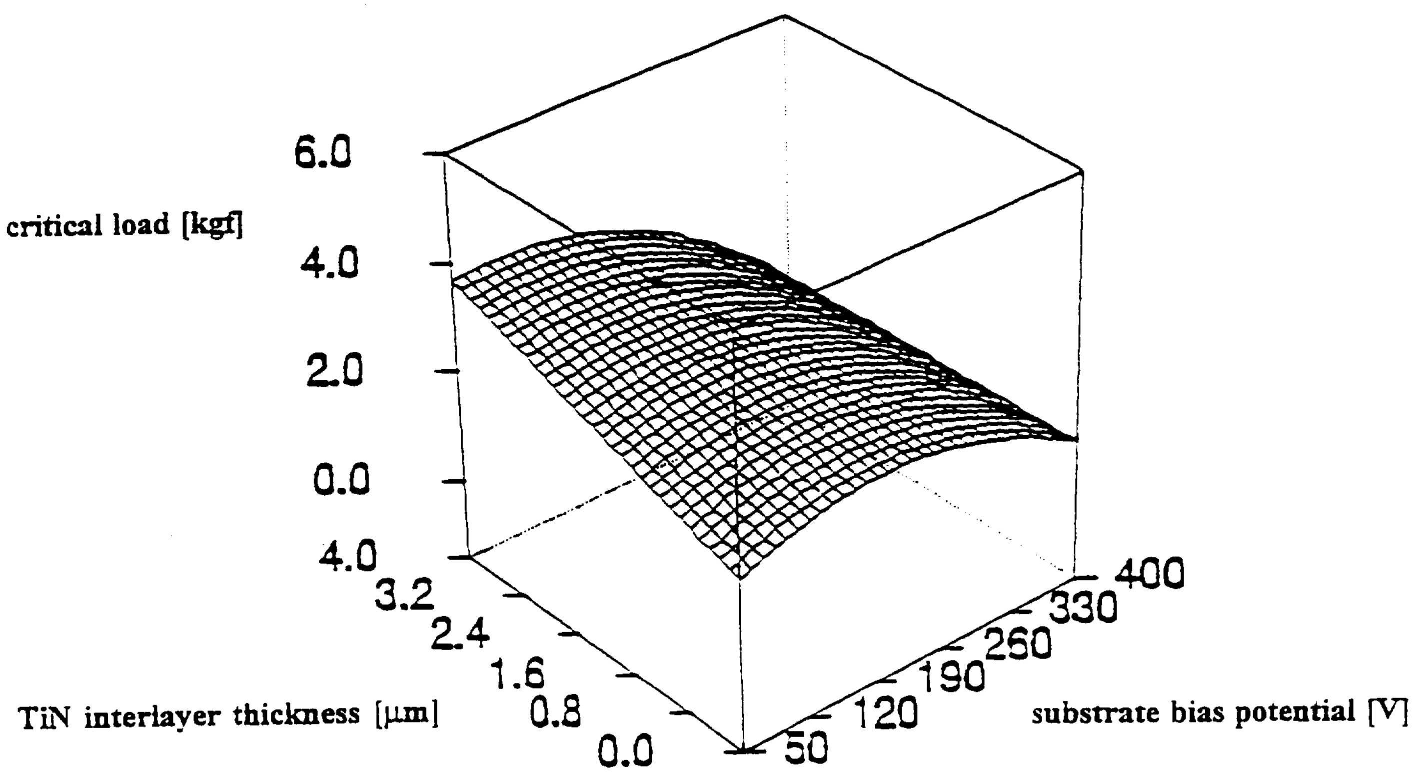

Figure 7. The three-dimensional adhesion response surface of the substrate bias potential and the TiN interlayer thickness at 3 mTorr nitrogen partial pressure.

Depending on the substrate bias voltage level and the nitrogen partial pressure, an adhesion enhancement of factor 4–6 times could be achieved by varying the interlayer thickness over the range of 0.001 to 4 μm. A linear relationship between the interlayer thickness and the adhesion response is observed, and the adhesion critical load increased as the interlayer thickness increased. Since the interlayer thickness did not exceed 4 μm in this work, it is not known if the optimum thickness has yet been found.

The influence of the substrate bias is characterized by a maximum in the adhesion response for an intermediate bias voltage. The maximum in adhesion is in the bias voltage range of -80 V to -250 V depending on the other parameters. For thick interlayers, the maximum adhesion value shifts towards smaller (absolute value) bias voltages.

The influence of the nitrogen partial pressure on the adhesion is small. As is shown in Figures 5 to 7, there was very little change in the critical load as the nitrogen partial pressure was changed from 1 to 3 mTorr.

The process parameter window for further investigation based on the adhesion response should be designed around a 4 μm TiN interlayer thickness and -120 V substrate bias. From this work, these conditions should give the best overall adhesion for the dual coating/substrate system.

Friction Coefficient Response Surface

For the friction coefficient response surface, a constant interlayer thickness of 4 μm was chosen as the basis for the calculation since this value gave the maximum in the adhesion response. The results from the study of the variation of the nitrogen partial pressure and the substrate bias voltage at a fixed interlayer thickness is shown in Figure 8. The lowest friction value of 0.1 between the CN_x coating and the 52100 steel counterpart was achieved with low or medium substrate bias voltage (-80 to -200 V) and a high nitrogen partial pressure of 3 mTorr. The process parameter window for further investigations, based on this friction coefficient response,

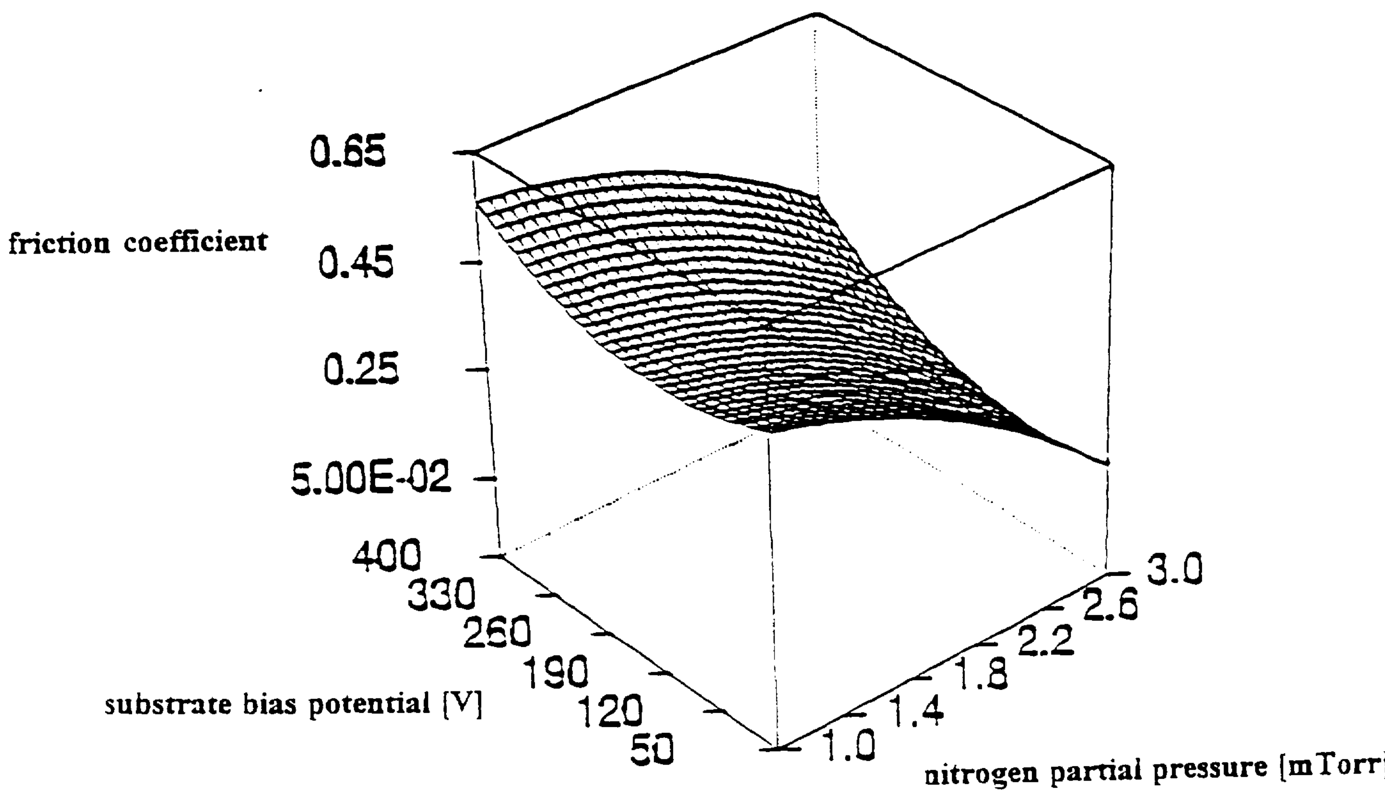

Figure 8. The three-dimensional friction coefficient response surface of the substrate bias potential and the nitrogen partial pressure at a TiN interlayer thickness of 4 μm.

should be designed around a -100 V substrate bias voltage and a 3 mTorr nitrogen partial pressure to achieve low friction.

The lowest friction coefficient for CN_x found in this work is excellent, and the value of 0.1 is comparable to other carbon based coatings. Typically coatings such as diamond-like carbon and metal containing diamond-like carbon coatings sliding against steel have friction coefficients[11] in the range of 0.1 to 0.4. Our material is on the low end of this scale and is very good.

Remarks

Summarizing the results of the response surfaces studied, the next parameter space investigated should look at interlayers greater than 4 μm in thickness. It is believed that there is a critical thickness where the adhesion response will be a maximum, but this maximum has not been observed yet. Increasing the interlayer thickness beyond that maximum point probably will decrease adhesion due to the high compressive stresses of the interlayer.

To improve the friction coefficient once the optimum interlayer thickness is established, the substrate bias voltage should be studied between -120 V and -80 V because it is in this range that we observe the lowest friction coefficients. In the present study, we did not find a minimum in the friction coefficient. It decreased as the nitrogen partial pressure increased from 1-3 mTorr. It is possible that the friction coefficient will continue to decrease as the nitrogen partial pressure is increased above 3 mTorr, and future work should investigate this possibility.

CONCLUSIONS

On the basis of the statistically designed experiments, the following conclusions can be drawn.

- Well adhered CN_x coatings can be deposited on 440C stainless steel with the aid of an TiN interlayer. Deposition of CN_x coatings without interlayers results in either spontaneous delamination or very low scratch adhesion values on the order of hundreds of grams.

- The dual coating/substrate composite always failed at the CN_x/TiN interface, independent of all of the variations of the deposition parameters.

- Independent of the substrate bias voltage value and the nitrogen partial pressure, the adhesion had a maximum value for the thickest interlayers investigated.

- The substrate bias voltage has an influence on the adhesion. The maximum adhesion is observed for coatings produced in a bias range from -80 to -250 V, depending on the nitrogen partial pressure and the interlayer thickness.

- Nitrogen partial pressure had little if any influence on the adhesion.

- The friction coefficients determined at a Hertzian pressure of 191 MPa and an interlayer thickness of 4 μm show a minimum value of 0.1 at high nitrogen partial pressures and substrate bias voltages in the range of -50 to -200 V.

- Statistically designed experiments were successfully applied to define a new production parameter space for CN_x coatings for future investigations.

FUTURE WORK

Based on this study, the following recommendations are made for future work in this area.

- Explore the promising process parameter area of high interlayer thickness of 4 μm or higher, intermediate substrate bias voltage region (-80 to -150 V), and high nitrogen partial pressure of 3 mTorr or higher to try to improve the sliding behavior and the load bearing capacity of the dual coating/substrate composite even further.

- Use advanced process control to enhance the sputtering process.

- Expand the deposition conditions to a higher hardness area of CN_x.

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