Refractory amorphous metallic $(W_{0.6}Re_{0.4})_{76}B_{24}$ coatings on steel substrates

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Refractory metallic coatings of $(W_{0.6}Re_{0.4})_{76}B_{24}$ (WReB) have been deposited onto glass, quartz, and heat-treated AISI 52100 bearing steel substrates by dc magnetron sputtering. As-deposited WReB films are amorphous, as shown by their diffuse x-ray diffraction patterns; chemically homogeneous, according to secondary ion mass spectrometry (SIMS) analysis; and they exhibit a very high ($\sim 1000\,°C$) crystallization temperature. Adhesion strength of these coatings on heat-treated AISI 52100 steel is in excess of $\sim 20\,000$ psi and they possess high microhardness (~ 2400 HV_{50}). Unlubricated wear resistance of such hard and adherent amorphous metallic coatings on AISI 52100 steel is studied using the pin-on-disc method under various loading conditions. Amorphous metallic WReB coatings, about $4\,\mu m$ thick, exhibit an improvement of more than two and a half orders of magnitude in the unlubricated wear resistance over that of the uncoated AISI 52100 steel.

INTRODUCTION

Several refractory metal-metalloid based metallic glasses, prepared by rapid quenching,[1] have exhibited high ($\sim 800\,°C$) crystallization temperatures and unique mechanical properties such as high hardness[2] and wear resistance, making them strong candidates as protective surface coatings. Applications of liquid-quenched amorphous metallic alloys as protective layers are, however, limited since liquid quenching can to date at the most yield amorphous alloys in the form of ribbons of only a few centimeters width. On the other hand, the application of magnetron sputtering technique to the synthesis of amorphous metallic alloys in thin film form offers a means of solving this problem since the technique allows uniform depositions over large areas. Furthermore, magnetron sputtering also offers an effective way to coat multicomponent materials at high rates with relative ease of control over the composition of the deposits, even beyond the equilibrium solid solubility limits, and in particular, under relatively low sputtering pressure (1–20 mTorr), yielding dense, void-free coatings.[3,4] Amorphous coatings of several metallic alloys have indeed been deposited by using the magnetron sputtering technique. Many of such amorphous coatings have exhibited[3,5-8] comparable, even superior in some cases, structural, mechanical, and chemical properties with respect to their liquid-quenched counterparts. Magnetron sputtered, amorphous films thus offer a possible alternative to the well-known polycrystalline coatings[9] of mechanically strong, hard, refractory materials, such as the nitrides and carbides of tantalum, titanium, zirconium, and silicon used primarily to reduce the wear of the surface in order to prolong the effective lifetime of the component.

Moreover, in the case of currently used polycrystalline coatings, the workpiece is usually heated to significantly high (600–800 °C) temperatures during the film deposition process. Partial interdiffusion at the interface of the overlayer and the workpiece yields the required adhesion. High-temperature deposition processes, however, are sometimes undesirable when dealing with delicate components of machinery with small dimensional tolerances.

It is possible to circumvent this problem with the magnetron sputtering technique, since the magnetic confinement of the plasma in the magnetron sputtering process offers an independent control over the substrate temperature. Furthermore, the high kinetic energy of the incident vapor flux and a suitable choice of substrate bias leading to energetic ion bombardment of the film being deposited, allows good adhesion of the deposited films on the surface without an appreciable rise in the temperature of the whole workpiece.

We have undertaken a study[3,5-8] of structural, mechanical, electrical, chemical, and magnetic properties of magnetron sputter deposited amorphous metallic thin films and their comparison with their liquid-quenched counterparts. In this paper, we report on the physical and mechanical properties of sputtered, amorphous coatings with a nominal composition of $(W_{0.6}Re_{0.4})_{76}B_{24}$ (WReB) deposited at low substrate temperatures ($< 150\,°C$) on AISI 52100 bearing steel. WReB films also exhibit remarkable chemical corrosion resistance in acidic and neutral aqueous solutions, which will be discussed elsewhere.

EXPERIMENTAL DETAILS

Films of amorphous metallic WReB, typically 2–5 μm thick, were deposited on glass, quartz, and AISI 52100 steel substrates using a dc, Research-S-Gun magnetron sputtering system. The target of $(W_{0.6}Re_{0.4})_{76}B_{24}$ was prepared from fine (< 125 mesh), high-purity (99.99%) powders of W, Re, and B. Appropriate amounts of the powders were thoroughly mixed together and then hot pressed at $\sim 1200\,°C$ under 3000-psi pressure for several hours to form the dense target. Substrates were mounted about 8 cm away from the target. Argon was used as the carrier gas for sputtering. Typical rate of deposition was ~ 300 Å/min. Details of the deposition procedure are reported elsewhere.[5] Compositional uniformity along the thickness of the films was studied

PIEZO ELECTRIC
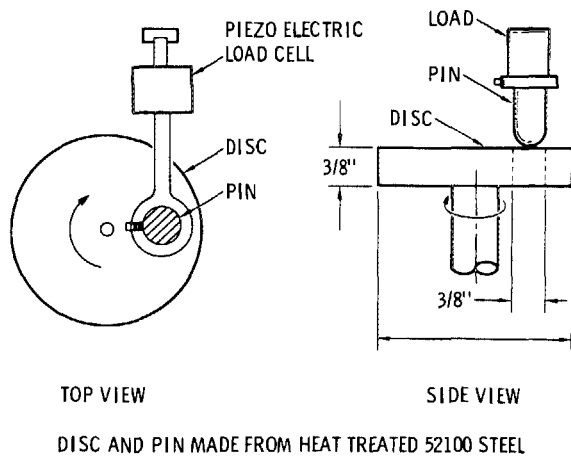LOAD CELL

DISC

PIN

TOP VIEW

LOAD

PIN

DISC

3/8"

3/8"

SIDE VIEW

DISC AND PIN MADE FROM HEAT TREATED 52100 STEEL

FIG. 1. Schematic diagram of the experimental setup for the "pin-on-disc" method of surface wear rate measurement.

$(W_{0.6} Re_{0.4})_{76} B_{24}$

FILM THICKNESS: 5.2 μm

RADIATION: Cu$K\alpha$

FIG. 2. X-ray diffraction pattern of a 5.2-μm-thick WReB film using Cu$K\alpha$ radiation.

using secondary ion mass spectrometry (SIMS) (Cameca, Inc., model 3f). Also, uniformity of the chemical composition over the film surface was verified by comparing the secondary ion mass spectra obtained from different spots on the film. Film thickness as well as depth of the craters created by sputter etching during the SIMS studies were measured for calibration purposes using a surface profilometer (Tencor, Inc., model Alphastep 100). The films deposited on glass and quartz substrates were utilized for the structural characterization by x-ray diffraction and the determination of the crystallization temperature (T_x). X-ray diffraction studies were performed on a Norelco "Theta-two theta" diffractometer using Cu$K\alpha$ radiation. Electrical resistivity of the films was measured as a function of temperature to obtain T_x. This was done by enclosing the sample in an inert atmosphere of argon in a temperature-controlled tube furnace. The sample resistance, measured by the four-probe method, was continuously recorded by a computer which also maintained a constant (~ 1.5 °C/min) heating rate for the sample by using the sample temperature as a feedback signal. Film adhesion strength to the substrate was estimated from the measurements of the force required to pull off epoxy-coated aluminum studs (Sebastian 1 test, Quad Group) attached to the film surface.

The substrates used for the hardness measurements and wear tests were heat-treated AISI 52100 bearing steel discs and pins. Both the disc (6.35 cm diameter, 0.953 cm thick) and pin (0.953 cm diameter with a spherical tip) were annealed at ~ 900 °C for 1 h and then quenched in water. The samples used in the wear tests were then tempered at 300 °C for 40 min resulting in a hardness of $59 \pm 3 R_c$ (Rockwell hardness on C scale). These heat treated pins and discs were then polished to better than a root-mean-square roughness of 1000 Å.

The Vickers microhardness tests on the coatings were carried out using a Leitz microhardness tester (diamond pyramid technique) with different loading conditions. Wear measurements were performed at room temperature, under atmospheric conditions using the pin-on-disc method[10] shown in Fig. 1. The pin-on-disc technique was selected for two reasons: it is sensitive under low load (< 1 kg) condi-
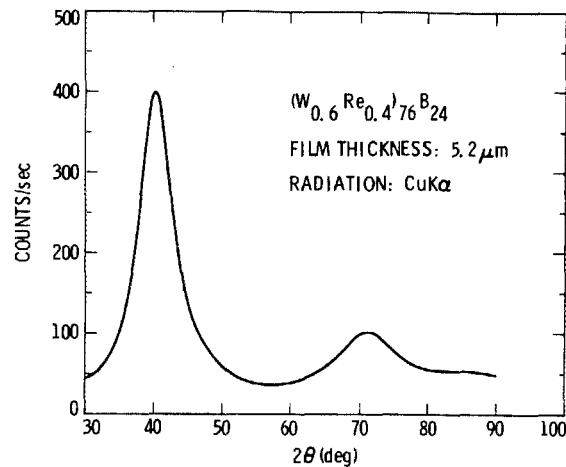
tions; and the volume loss from the pin, a direct measure of the wear, can be conveniently obtained from the diameter of the wear pattern on the pin. The sliding speed of the pin on disc was maintained constant (~ 30 cm/s) by adjusting the disc rpm. The wear pattern as well as the volume loss of material from the pin was then studied as function of the sliding distance and the load. A maximum load of 1 kg was used. Typical testing times of 1 h at 5-cm nominal diameter were utilized. The volume removed was calculated by measuring the mean diameter of the wear spot on the spherical surface of the pin. To optimize the wear characteristics of the coated pin and disc with respect to those of the uncoated pin and disc, effects of the following sputtering parameters on the wear behavior were systematically studied: argon pressure, sputter etching of the substrates prior to the actual deposition, substrate bias during deposition, and substrate temperature.

RESULTS AND DISCUSSION

Figure 2 shows an x-ray diffraction pattern from an as-deposited 5.2-μm-thick WReB film on glass using Cu$K\alpha$ radiation. The broad diffraction band and absence of any sharp lines in the pattern are typical characteristics of all amorphous materials. A typical composition depth profile by SIMS of an as-deposited WReB film ($\sim$ 0.8 μm thick) is shown in Fig. 3. Uniformity of the composition throughout the film thickness is remarkable. The drop in the profiles at ~ 0.8 μm is due to the film-substrate interface. It must be mentioned, however, that several initial deposition runs from the new target showed significant composition variations along the film thickness presumably due to the differences in sputtering yields of the constituents. Only after long conditioning of the target (corresponding to almost 1-mm erosion of the target surface) did film composition stabilize and show reproducibility from run to run. In every run, however, the target was routinely presputtered onto a mechanical shutter for several minutes before exposing the substrates to the vapor flux. Also, the amorphous nature and composition uniformity of the films were closely monitored for variations during the entire course of the work, especially when-
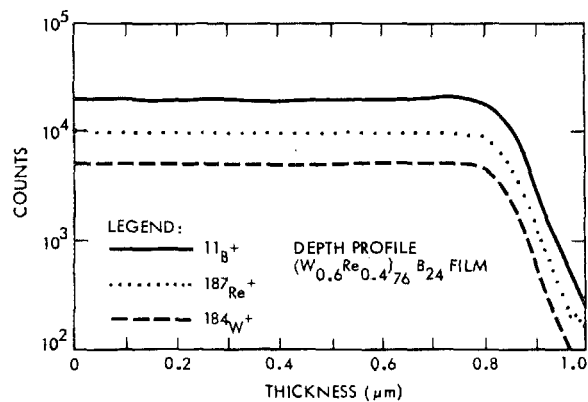
FIG. 3. Chemical composition-depth profile of a WReB film on glass using secondary ion mass spectrometry.

FIG. 4. Temperature dependence of the normalized resistivity for a WReB film. The sharp drop in resistivity at ~ 1275 °K corresponds to the crystallization of the film.

ever sputtering conditions were changed. No significant variations were observed.

The temperature dependence of the normalized resistance of a film deposited on quartz substrate heated at a constant rate (~ 1.5 °C/min) in an inert atmosphere of argon is shown in Fig. 4. The large, irreversible change in the film resistance at about 1275 °K corresponds to the crystallization of the film as verified by its x-ray diffraction analysis.

Although overall chemical homogeneity, noncrystalline nature, and crystallization temperature of the films showed little dependence on the deposition conditions, film microstructure and surface texture, frozen-in stress distribution in them, their adhesion strength, their apparent hardness, and their wear characteristics exhibited sensitive functional dependence on the sputtering parameters. Therefore, to investigate the real potential of such a material as a protective coating, it was necessary to establish the correlations among the deposition conditions, film microstructure, and its useful properties. A brief discussion on the influence of some of the most determinant deposition conditions is presented below.

The carrier gas (Ar) pressure had the most dominant influence on both the microstructure and the internal stresses in the films. WReB films deposited at room temperature on AISI 52100 steel at low (< 8 mTorr) argon pressure possessed a mirror-smooth surface finish. However, they exhibited blistering-induced delamination from the substrates when exposed to the atmosphere indicating the presence of very high compressive stresses in them. On the other hand, films deposited at pressures of ~ 15 mTorr and above contained a high density of tensile stresses causing adhesion failure through a gradual development of numerous random microcracks in them. Such a transition from the compressive to tensile stress with increasing carrier gas pressure has been observed in a large variety of polycrystalline as well as amorphous thin films deposited by cylindrical and planar magnetron sputtering.[11,12] The films deposited at higher pressures (> 15 mTorr) were also characterized by rough, nonreflecting surface and columnar microstructure as seen in scanning electron micrographs of the film cross sections. This columnar microstructure formed at higher deposition pressures is consistent with Thornton's zone structure diagram[13] and corresponds to its zone 1 characteristics. Adherent films with low internal stresses and dense void free microstructure
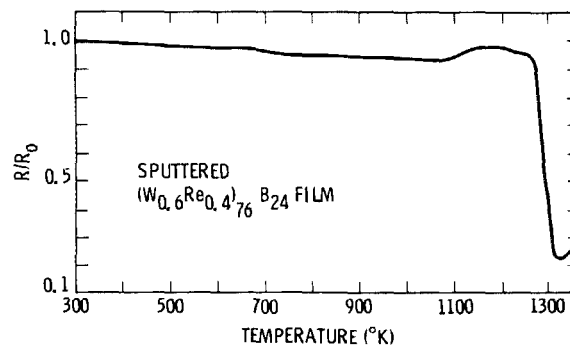
were obtained at ~ 10 mTorr argon pressure, a point within the transition region between the high compressive and high tensile stress regimes. A detailed quantitative discussion of the internal stresses in such amorphous alloy films deposited at various pressures is presented elsewhere.[8]

The films with low internal stress levels were subjected to the pull test to determine their adhesion strength. Films deposited at room temperature, without any sputter etching of the substrates, exhibited rather poor adhesion values (~ 1000 psi), presumably due to the abrupt nature of the film-substrate interface. Significant improvement in adhesion (6000–8000 psi) was observed when the steel surface was subjected to a light sputter etch just prior to the film deposition. This was accomplished by maintaining the substrates at − 500 V dc bias in ~ 50 mTorr pressure of argon, resulting in about 0.5 mA/cm^2 current density, for 10 min. In addition to the removal of any surface contamination layer, if present, an adsorbed gas layer, and the surface oxide layer; sputter etching also creates a large density of surface defects which increases the nucleation density, thereby reducing the number of voids at the interface.[14] The rough surface texture created on the steel is also expected[15] to inhibit the interface crack propagation leading to delamination.

Furthermore, the negative substrate bias was maintained during the initial few minutes of actual deposition with the intent that Ar$^+$ ion bombardment of the substrates and the resulting partial sputter etching of the growing film would help to reduce the developing stresses at the incoherent substrate-film interface. Messier et al.[16] have recently illustrated through a revised zone structure model that such an ion bombardment also increases nucleation density for incident atoms, reduces surface roughness by eroding fast growing peaks in the coating, and therefore can suppress the growth of undesirable zone 1 structure. Ion bombardment however is more effective in supressing the influence of substrate and film roughness at higher carrier gas pressures[17] and requires backsputtering of a significant fraction of the incident flux before the beneficial effects are seen. This also reduces the net deposition rate substantially. In the present study, the distinct overall effect of the substrate bias during the initial stages of film growth was a further remarkable increase in the film adhesion strength to more than ~ 20 000 psi (> 1.4 × 10^8 N/m^2), presumably due to the formation of a less abrupt, interdiffused interface. The actual film adhe-
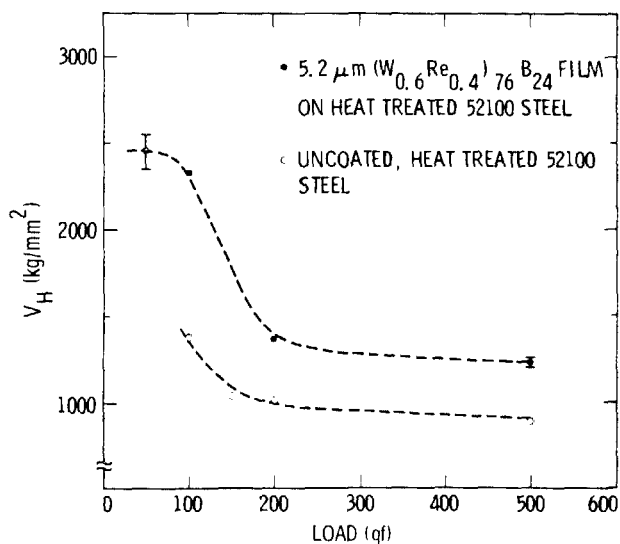
FIG. 5. Vickers microhardness as a function of load for a 5.2-μm-thick WReB film on heat-treated AISI 52100 steel. Hardness of the uncoated steel surface is also shown for comparison.

sion strength was in fact even higher than the recorded values and could not be measured with the present pull test because of the reproducible failure (at ~20 000 psi) at the epoxy/film interface instead of the film/substrate interface.

An important purpose of this work was to avoid excessive heating of the workpiece during the film deposition. Substrate temperature during ion bombardment and/or actual deposition did not exceed ~150 °C, according to a chromel-alumel thermocouple attached to the front surface of a control sample. However, to study the effects of a simultaneous application of a negative bias and heat to the substrates during the film growth, films were deposited at different substrate temperatures up to ~400 °C. Substrate heating was achieved by controlling the input power fed into a quartz halogen-radiation heater mounted with a parabolic molybdenum reflector facing the substrates in the sputtering chamber. Substrate temperatures up to 400 °C resulted in amorphous films according to their x-ray diffraction patterns, however, effective deposition rate dropped significantly at temperatures above ~350 °C indicating a drastic reduction in the sticking coefficients of the elements at higher temperatures. Films deposited without substrate bias showed some improvement in their adhesion strength with increasing substrate temperature. Biasing of the substrates on the other hand, at room temperature as well as at elevated temperatures, resulted in significantly higher adhesion (> 20 000 psi) strengths. This implies that, as compared to the whole workpiece heating, ion bombardment of only the surface during the initial stages of the nucleation and film growth is significantly more effective and energy efficient in forming a properly intermixed interface. Possible improvements in the mechanical properties such as hardness and wear resistance of liquid-quenched metallic glasses have been suggested[18] by adjusting the initial quenching rate and/or reheating the as-quenched glass beyond its glass transition temperature causing partial recrystallization. Such a treatment however would certainly defeat the basic

advantage of the near room temperature deposition in the present case.

Microhardness for various values of load is shown in Fig. 5 for an as-deposited, 5.2-μm-thick, amorphous WReB film on an annealed (~900 °C, 1 h) but untempered AISI 52100 steel disc (with hardness R_c ~67). The high hardness value of the substrate was found to be particularly useful in obtaining film hardness as discussed below. As seen in Fig. 5 for both coated and uncoated surfaces, the well known near surface effect in hardness measurements generally causes the hardness number to increase with decreasing load below a certain critical threshold. However, the coated sample exhibits an equilibrium hardness value (no more increase with decreasing load) below ~75 gf which then may be attributed to the film material. Also, the indentation depths in this region are less than ~25% of the film thickness. The film hardness is therefore ~2400 kg/mm^2 (2400 HV$_{50}$). For a film deposited onto an annealed and tempered substrate (R_c ~59) on the other hand, the hardness value of ~2400 kg/mm^2 was indeed observed but at much lower loads (15-25 gf) with increasing scatter and without an unambiguous equilibrium value.

The microhardness value for a metallic glass of identical chemical composition is unavailable for comparison. Nonetheless, the hardness value of amorphous thin films of different MoRu-based alloys measured at low load equilibrium points and the hardness values of their thicker, liquid-quenched counterparts measured at high equilibrium loads, compare very well. The present value of 2400 kg/mm^2 is significantly higher than not only that of a variety of liquid-quenched Fe-, Co-, Ni-, and Pd-based glasses (325–1400 kg/mm^2)[19] but also that of Mo-Ru and W-Ru based glasses (up to 2000 kg/mm^2).[2]

Wear rate of an as-deposited, 4-μm-thick, WReB film on a heat-treated AISI 52100 steel pin on a similarly coated steel disc for various load values at a constant sliding speed of 30 cm/s is plotted in Fig. 6. Also included in the figure is the wear rate for an uncoated, heat treated, AISI 52100 steel pin on uncoated disc under identical running conditions. It is clear from the figure that coating the AISI 52100 bearing steel surface with an amorphous WReB film reduced its effective wear rate by almost 2 1/2 orders of magnitude.

It is a well-known fact in the tribology community that due to the sensitive dependence of the values of any tribological parameter on the measurement technique employed and the conditions selected, comparison of the results from different investigators and laboratories is a perpetual problem. The unavoidable large scatter in the tribology data complicates the analysis even further. Moreover, wear resistance of metallic glasses has attracted attention only recently. The literature on the wear characteristics of amorphous metallic alloys[18,20–23] is therefore limited to only a few, and mostly, liquid-quenched glasses; leaving very little for direct comparison. Nevertheless, an attempt has been made in the following to generate some qualitative understanding of the observed wear behavior of the sputter-deposited amorphous coating.

The wear rate of WReB increased with increasing load as is also observed[23] in other amorphous alloys. When plot-
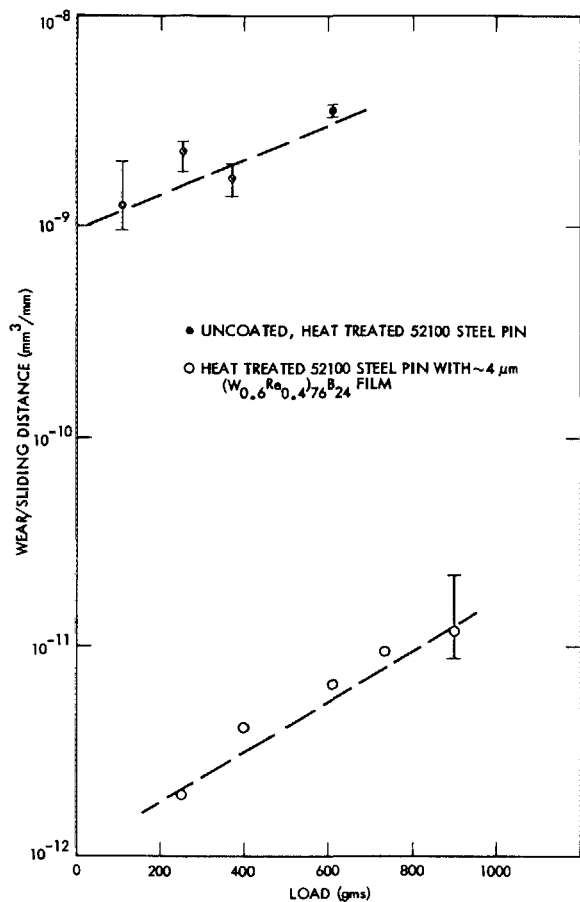
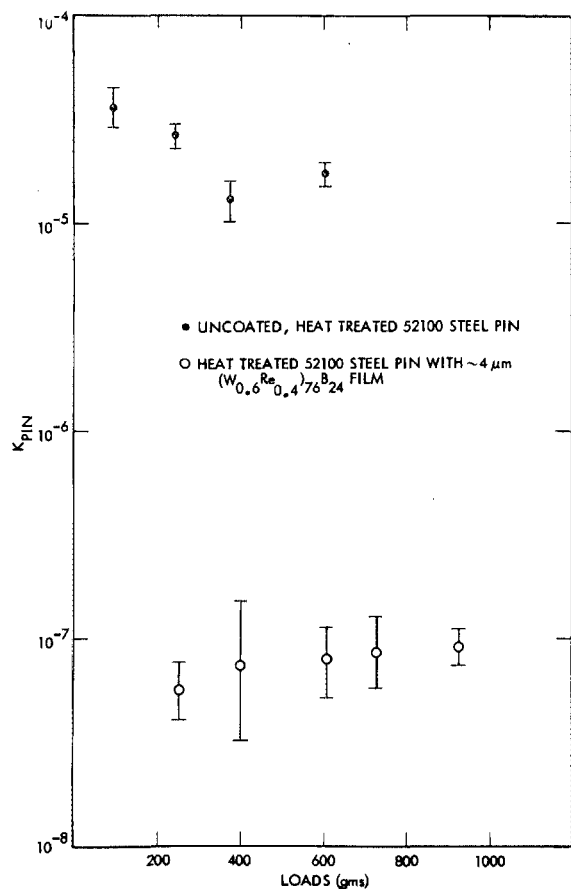FIG. 6. Wear rate as a function of load for the WReB-coated and uncoated steels.

FIG. 8. Wear parameter K_{pin} as a function of load for the WReB-coated and uncoated steel surfaces.
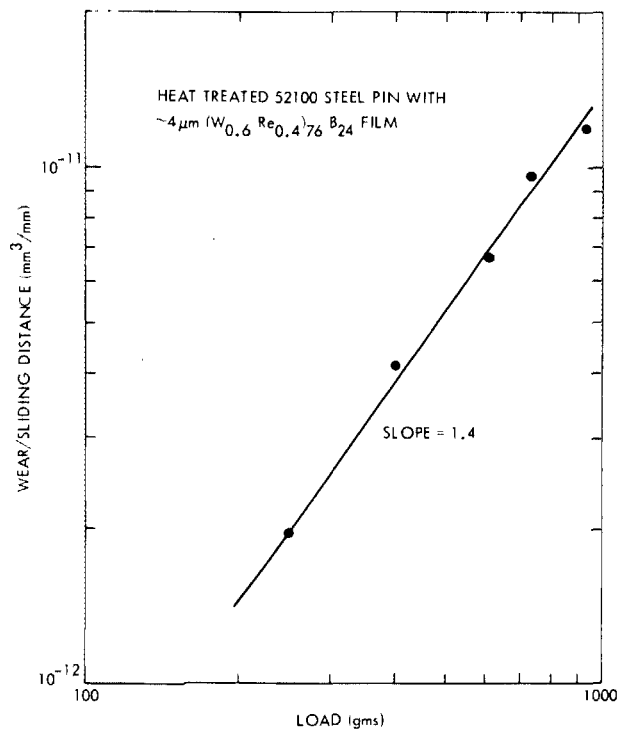

FIG. 7. Log-log plot of the wear rate vs load for the WReB-coated steel surface.

ted in a log-log form (Fig. 7), the data yield a straight line with a slope of ~ 1.4, which indicates a near-linear dependence of the wear rate (W) on load (P). Complex mechanisms of wear involved in amorphous metals have not yet been uniquely identified. In fact, different amorphous metallic alloys have displayed totally contradictory characteristics. For example, both increase[23] as well as decrease[18] in wear rate with increasing sliding speed have been observed in amorphous alloys.

When compared with the behavior of crystalline metals, the near-linear dependence of the wear rate of WReB on load suggests the model of adhesive wear[24] may be applicable to the present case. The near-linear dependence on the load also indicates that the ultimate wear debris may have been formed through the lump removal process by plastic deformation.[25]

In the adhesive wear model, two surface asperities, coming in intimate contact, form a pseudo-weld. Further relative motion then results in either failure of the newly formed joint or fracture of the segment of one of the asperities resulting in metal transfer. This process may be applicable to amorphous metals since they are known[7] to possess an extremely thin (only a few monolayers), homogeneous, chemically passive surface oxide layer on them which gives rise to their remarkable chemical corrosion resistance.[7,8] However, such a fragile oxide layer remains extremely susceptible to breakage on a sliding contact, exposing the pure alloy and thereby increasing the possibility of adhesive wear. Such a material

transfer could result in an increased surface roughness, and the large asperities thus formed may subsequently initiate the plastic deformation wear by lump removal.

The adhesive wear process is generally described using the adhesive wear coefficient K, a probability factor which determines whether a given contact would result in a wear particle. It ranges from 10^{-3} to 10^{-7} in crystalline metals for the adhesive wear case, in contrast with the very high values of K ($10^{-1}-10^{-3}$) observed for the abrasive wear case.[24] The wide ranging values of K in any given model indicate[24] that any particular type of wear always embodies many submechanisms, the precise details of which are difficult to analyze. The experimental value of K may therefore only be considered as an approximate indication of the most dominant mechanism. Using the expression for $K_{pin} = 3HW/P$, derived for the case of adhesive wear,[26] where H is the hardness in kg/mm^2, W is the wear rate in mm^3/mm, and P is the load in kg; the calculated values of K_{pin} for uncoated and WReB-coated surfaces are plotted in Fig. 8. The dependence of K_{pin} on load for a coated surface diminishes at the higher values of load, and approaches a constant value, as predicted by the lump removal mechanism based on plastic deformation.[25] On the other hand, it continues to decrease for the uncoated crystalline surface.

A large range of K values for steel surfaces has been reported[27] in the literature, particularly for varying carbon content. The value obtained for the uncoated AISI 52100 steel in the present work is somewhat lower. However, the purpose of this paper is only to present the relative difference between the wear behavior of uncoated and amorphous WReB-coated steel and show the potential of hard, adherent amorphous metallic films as wear resistant protective coatings.

CONCLUSIONS

Chemically homogeneous, amorphous films of refractory metallic $(W_{0.6}Re_{0.4})_{76}B_{24}$ (WReB) alloy have been deposited onto AISI 52100 bearing steel by magnetron sputtering. Under optimized deposition conditions, they exhibit a dense, void-free microstructure; a high (~ 1000 °C) crystallization temperature; adhesion strength in excess of 20 000 psi ($> 1.4 \times 10^8$ N/m^2); and Vickers microhardness of 2400 kg/mm^2 (2400 HV$_{50}$) Amorphous WReB coatings about 4 μm thick on heat-treated AISI 52100 steel show an improvement of more than two and a half orders of magnitude in the unlubricated wear resistance over that of uncoated AISI 52100 Steel. Comparison of the data with models for the wear of crystalline metals suggests the wear mechanism in WReB may be that of adhesive wear with lump removal based on plastic deformation. The direct comparison with crystalline models, however, must be used cautiously since the absence of grain boundaries, slip planes, stacking faults, dislocations, and anisotropy normally found in crystalline materials could significantly change the mechanisms of wear in amorphous coatings.

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