The method includes the steps of forming titanium oxide layer on the surface of the titanium or the titanium alloy, coating the titanium oxide layer with a composition comprising an epoxy resin and curing the epoxy resin. The materials employed to make the coating of the present invention may also be employed in the method of the present invention.

EXAMPLES 1–3 AND COMPARATIVE EXAMPLES A–D

A set of modified four-ball wear tests was used to evaluate the tribological properties of the coating of the present invention on titanium and its alloys. The modified four-ball wear tests employ a "BTF" (ball-on-three flats) geometry, that is, one Ti—6Al—4V alloy ball of 12.70 mm diameter is rotated on three stationary titanium flats of ASTM Grade 2 purity. The tests were conducted with the top ball rotating at 200 rpm (7.6 cm/sec) at room temperature. Each test lasted for 30 minutes. The wear scar diameters on the flats were measured by an optical microscope. The friction coefficients were calculated based on the recorded frictional torques, which were measured by a strain gauge attached to the wear tester.

The titanium flats of 6.35 mm diameter were polished to a "mirror surface" finish with a final thickness of 1.6 mm. Variation in thickness for the three flats was within 0.01 mm. Prior to each test, both the ball and the flats were thoroughly cleaned in an ultrasonic bath with hexane, acetone and 5% detergent in deionized water.

For pretreatment, the cleaned titanium specimen was first immersed into a 2% solution of TYZOR® TBT (tetra-n-butyl tinanate ex. Du Pont) in heptane. After evaporation of heptane, the TBT was quickly hydrolyzed by moisture in the air to form a thin, dense network of titanium dioxide film. Two brands of glycidyl resin, supplied by Buehler and Dow Chemical USA, respectively, were used for the coating. Buehler epoxy resin consists of his-phenol A epoxy resin (i.e. 4,4'-isopropylidene-bis-phenyl diglycidyl ether) and n-butyl glycidyl ether. Coating of Buehler epoxy resin was conducted by immersing the above-described dioxide coated specimen into the liquid resin (1/5 resin weight of "Epo-Kwick™ Hardener" added). The hardener is a mixture of three amines (diethylenetriamine, triethylenetetramine and polyoxypropylenediamine). Cure was carried out at room temperature overnight. Dow Epoxy-Novolac (DEN) 431 and 438A85 resins contain 2.2 and 3.6 epoxy groups per molecule respectively. The multifunctionality permits upgrading of thermal stability, chemical resistance, and electrical and mechanical properties of bis-phenol A-epoxy polymers. Coating of DEN resins was carried out on a hot plate at about 100° C. and the curing agent used was EMI-24 (2-ethyl-4-methylimidazole). Final curing was carried out at 160° C. for 20 hours. In the latter case, a higher curing temperature of 160° C., rather than room temperature, was applied in order to achieve high thermal and chemical degradation stability and a higher heat deflection temperature.

Coating of titanium and/or its alloys while using PPO as lubricant gave an extremely low wear with an extremely low friction coefficient (FC), greatly surpassing any test results of uncoated titanium flats with any lubricant, including the test with hexachloro-1,3-butadiene as lubricant (See Table 1). Comparing the recorded frictions in FIG. 1, the different tribiological features between the coating and the uncoated Ti—6Al—4V ball to pure titanium are readily apparent. The severe "stick-slip" phenomenon in uncoated samples strongly indicated ineffectiveness of lubrication and a high propensity of titanium for galling and grooving.

TABLE 1

Four ball wear test result
(loading: 5 Kg/200 rpm/room temperature/30 min)

Example	Ti-6A1-4V Ball	Ti (grade 2) Flats	Lubricant	WSD (mm)	FC
A	uncoated	uncoated	none (air)	3.56	0.41
B	uncoated	uncoated	poly (propylene glycol)	2.37	0.35
C	uncoated	uncoated	hexachloro-1,3-butadiene	0.79	0.094
D	uncoated	uncoated	PPO	3.69	0.45
1	uncoated	Buehler Epoxy-coated	PPO	2.67	0.04(2') 0.16(3') 0.28(3') 0.35(17')
2	uncoated	Dow 438-A85 coated	PPO	1.79	0.05(2') 0.21(4') 0.35(6')
3	Dow 438-A85 coated	Dow 438-A85 coated	PPO	0	0.047

FC = Friction coefficient. For Examples 1–2, the friction coefficient is given at several time intervals.
PPO = Polypropylene oxide
WSD = Wear scar diameter
Ti-6A1-4V is a titanium, aluminum and vanadium alloy.

EXAMPLES 4–15

In order to dramatically extend the lifetime of the coating, 2% (by weight) of diamond powder with a particle size of 0.001 to 1 μm was added as anti-wear filler and dispersed in the DEN438A85 resin before curing. The mixture was then coated and cured on the surface of Grade 2 pure titanium flats. The degree of curing, however, decreases as powdered diamond is added due to decreased molecular motion caused by the absorption of resin molecules on the diamond surface. For a diamond-filled epoxy resin, an elevated curing temperature is particularly critical to promote complete curing. The maximum thickness of the coating was 0.25 mm. The ball to flats wear tests in a step-loading sequence showed that up to 295 hours of accumulated test time, when the durability test was terminated, for each loading step after reaching a steady state very low wear and a very low friction coefficient were essentially preserved. The results are given in Table 2.

TABLE 2

Results of durability test on Four Ball Wear Tester
(ball: uncoated Ti-6Al-4V; flats: ASTM grade 2 pure Ti coated by Dow epoxy-novolac DEN438-A85 blended with 2% diamond powder (0–1 micron) anti-wear filler; speed; 200 rpm/r.t./lubricant: PPO)

Example	Loading (Kg)	Cumulative Time (hrs)	Friction Coefficient	WSD (mm)
4	5	11	0.09	1.49
5	5	21	0.09	1.55
6	5	40	0.09	1.60
7	5	60	0.09	1.47
8	5	80	0.09	1.50
9	5	200	0.09	1.47
10	10	200 + 5	0.11	1.57
11	10	200 + 25	0.11	1.53