ENERGETIC PARTICLE SYNTHESIS OF METASTABLE LAYERS FOR SUPERIOR MECHANICAL PROPERTIES


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ABSTRACT

Energetic particle methods have been used to synthesize two metastable layers with superior mechanical properties: amorphous Ni implanted with overlapping Ti and C, and amorphous diamond-like carbon (DLC) formed by vacuum-arc deposition or pulsed laser deposition. Elastic modulus, yield stress and hardness were reliably determined for both materials by fitting finite-element simulations to the observed layer/substrate responses during nanoindentation. Both materials show exceptional properties, i.e., the yield stress of amorphous Ni(Ti,C) exceeds that of hardened steels and other metallic glasses, and the hardness of DLC (up to 88 GPa) approaches that of crystalline diamond (~100 GPa). Tribological performance of the layers during unlubricated sliding contact appears favorable for treating Ni-based micro-electromechanical systems: stick-slip adhesion to Ni is eliminated, giving a low coefficient of friction (~0.3-0.2) and greatly reduced wear. We discuss how energetic particle synthesis is critical to forming these phases and manipulating their properties for optimum performance.

INTRODUCTION

Energetic particle methods are widely used to synthesize materials with special properties. The energies of impinging atoms vary greatly, from 100's of keV for ion implantation down to a few eV for plasma depositions [1]. We have used such methods to explore synthesis of two types of metastable layers with very high hardness and strength. First, ion implantation of Ti plus C into Ni with overlapping concentrations of ~20 at.% forms an amorphous phase [2]. Second, deposition of C at ~100 eV produces a hard, covalently bonded amorphous material known as diamond-like carbon (DLC) [3]. We have developed methods to quantify accurately the yield strength, elastic modulus and intrinsic hardness of these sub-micrometer layers on soft substrates for the first time: finite-element modeling is used to simulate and fit the response of the layer-substrate combinations to ultra-low load indentation, or "nanoindentation". We show that amorphous Ni(Ti,C) has exceptional strength for a metal, exceeding that of hard bearing steels, and that DLC can have hardness approaching that of crystalline diamond. This method is detailed elsewhere [4,5] but considerations specific to these two materials are given here.

Energetic particles are essential for producing these materials because the kinetic energy of the atoms forces them into the layer being formed, as opposed to being deposited on the surface with only thermal energy, and the additional energy can modify the atomic structure. The modifications range from atomic displacements and rearrangements at high energy to breaking and re-forming bonds at low energy. We show how mechanical properties can be manipulated by varying particle energies and other methods to optimize the structure and performance of each material. One motivation for our work is improved tribological performance of Ni components in micro-electromechanical systems (MEMS) [6,7]. Both layers give sizable reductions in friction and wear of Ni, and the two synthesis methods appear compatible with Ni-based MEMS.
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AMORPHOUS Ni(Ti,C)

Previously, the ion implantation of Ti and C into steels was examined extensively for reducing friction and wear [8,9]. To the best of our knowledge, this treatment produced benefits for every steel tested, as well as a Co-based alloy [10]. A key feature of the treatment was the formation of an amorphous surface layer, whose presence was found to correlate directly with the benefits obtained [11]. In addition, Ti + C implantation was found to amorphize Ni [12]. With the recent interest in using x-ray lithography to form high-precision, miniature molds and electroplating to invest them with Ni alloy (German process acronym LIGA [1,2]), we have examined Ti + C implantation of Ni as a treatment to improve the performance of Ni-based MEMS. Our recent work with pure Ni quantifies the intrinsic mechanical properties of the amorphous phase for the first time, and also evaluates the treatment of electroformed Ni for MEMS.

Microstructure and Composition of Ni Implanted with Ti and C

High-purity (99.995) Ni was annealed at 1000°C for 2 hours in a high vacuum of ~10^{-5} Pa (~10^{-7} Torr) to remove lattice damage. The anneal produced grain growth to sizes of several tenths of a millimeter and also grain relief. Specimens (12 mm x 12 mm x 250 µm) were polished with diamond suspensions down to 0.25 µm to obtain a mirror finish without relief, and then re-annealed. Titanium was implanted to a fluence of 2x10^{17} Ti/cm² at 180 keV which is predicted by TRIM97 [13] to give a projected range (Rp) of 62 nm. Carbon was then implanted to 2x10^{17} C/cm² at 45 keV for an expected Rp = 58 nm. These implantations produce nearly overlapping profiles of Ti and C, as seen with 6 MeV ^4He backscattering spectrometry in Fig. 1.

Plan-view transmission electron microscopy (TEM) showed that the implanted layer was only partially amorphous with remaining fcc Ni nanocrystals [14]. To determine the depth-dependent microstructure precisely, cross-section specimens were made by sandwiching the Ni between Si, extracting a cylindrical core centered on the implanted layer, slicing a disk from the core, and using metallographic polishing and ion milling to produce thin area including the implanted layer [15]. The microstructure of the layer is seen in Fig. 2: a sub-surface, fully amorphous layer that extends from 30 nm to 80 nm in depth (layer II), with a two-phase layer of
amorphous alloy with embedded Ni crystallites above it (layer I). Careful examinations of this and other images also reveal a thin (~6 nm) oxide at the surface. Beneath layer II is a highly dislocated layer extending from 80 to 180 nm (layer III); its deep boundary is somewhat difficult to identify in Fig. 2 due to damage in the Ni substrate from ion milling, but becomes apparent when wider areas are examined. The dislocations in layer III are due to ions in the tail of the implanted distribution extending into the Ni (see Fig. 2). Dark-field imaging with fcc Ni reflections and the diffuse ring of the amorphous phase confirmed these identifications and allowed us to estimate that the fraction of fcc material in layer I is ~20 vol.% [15].

By combining the depth variations of composition (Fig. 1) and microstructure (Fig. 2), the solute concentrations for amorphous phase formation can be identified. Between layers I and II, the C concentration falls from 22 to 16 at.% for a nearly constant Ti concentration of 16-18 at.%; the minimum composition for single-phase material thus lies between these limits. In the center of layer II, 22 at.% C and 16 at.% Ti give fully amorphous material. Beneath layer II, an abrupt transition occurs from amorphous alloy to crystalline fcc metal with 14 at.% C and 10 at.% Ti. Two additional pieces of information support our interpretation that the two-phase alloy in layer I forms due to insufficient C. First, the amount of lattice damage during the C implantation is sufficient for amorphization; TRIM97 simulations [13] predict ~100 dpa, so that even the last 1/10th of the C implantation produces sufficient displacements. Second, when a low-fluence implantation of 3x10^16 C/cm² is added at the lower energy of 20 keV (R_p = 28 nm) to introduce additional C into layer I, the implanted region is fully amorphous to the surface. This second implantation was applied to layers for sliding contact testing, since the poor tribological properties of untreated Ni suggest that the fcc crystallites would impair performance. Thus the metallurgy of Ti+C -implanted Ni can be assessed by combining ion beam analysis with TEM, and manipulated by adjusting ion energies to improve mechanical properties.

Composition limits have been studied more extensively for amorphous Fe implanted with Ti and C [16], and indicate that minimum C concentrations decrease with increasing Ti content. For our Ni alloy with 16 at.% Ti, an increased C content is needed relative to Fe: ~20 at.% C is needed for Ni, whereas ≤ 10 at.% C is required for Fe. This finding can guide composition choices in future work; a similar trend of decreasing C with increasing Ti is likely to be found for amorphous Ni(Ti,C) also.

Mechanical Properties of Bulk Ni Implanted with Ti and C

Mechanical properties of amorphous Ni(Ti,C) were evaluated by nanoindentation of annealed, high purity Ni implanted with Ti and C as in Figs. 1 and 2. Typical indenter force versus depth data are shown in Fig. 3 for indentation to 70 nm depth, near the center of the implanted layer. The dashed lines show the standard deviation of the data obtained for 10 indentations. The methods used to produce the fitted simulation shown in Fig. 3 are discussed in detail in [5,14]. Most of our modeling of hard-layer indentations results in deduced properties with absolute uncertainties judged to be about 10% or less, but this structure requires greater attention to obtain an accurate assessment. Careful examination of the indentation response data and attempts to fit it at all depths indicate the presence of a softer surface layer and a hardened layer extending beyond 100 nm depth where the implanted Ti and C concentrations are much reduced from their peak values (Fig. 1). The cross-section image in Fig. 2 shows the same features, and layers I (softer, 2-phase), II (fully amorphous, expected to be hardest) and III (reduced hardness, extends to 180 nm) were assigned separate properties in the model. In addition, knowing the depth intervals of layers I, II and III from TEM allows more accurate
modeling of multiple layers with fewer variables to be fitted. The fitted simulation determined a yield stress $Y.S. = 4.70 \pm 0.13$ GPa and an elastic modulus $E = 416 \pm 104$ GPa for amorphous Ni(Ti,C). The "intrinsic hardness" (independent of substrate) of the amorphous phase was determined by an additional simulation for a hypothetical "bulk" material with these values of $Y.S.$ and $E$ that gave $H = 13.7 \pm 2$ GPa.

These values greatly exceed those of pure Ni, as seen in Fig. 4. The $Y.S.$ is 30 times that of Ni ($0.15$ GPa) and the elastic modulus is doubled, producing an order of magnitude increase in hardenss. The values also exceed those of hardened 440C bearing steel and hard amorphous Fe-Ni stabilized by B additions. Such metalloid-stabilized amorphous phases typically have high hardnesses in the range 7 - 11 GPa due to the absence of crystallinity and associated plastic deformation by dislocation glide \[17\]. We hypothesize that the increased hardness of amorphous Ni(Ti,C) is due to a high concentration of Ti atoms that bond to C in the amorphous matrix. Evidence for this hardening is reported for melt-quenched alloys for which up to 2 at.% Ti was retained in solid solution and increased hardness by about 1 GPa \[18\]. Extrapolating this increment to our alloy with 16 at.% Ti predicts a hardness of $\sim 15$-19 GPa, reasonably accounting for our observed value. It is notable that amorphous alloys with such high Ti content are not attainable by melt quenching, even by very rapidly quenching with pulsed lasers \[19\], whereas they are readily formed by ion implantation and by pulsed-laser deposition \[20\].

Tribological improvements obtained with the amorphous layer under representative MEMS operating conditions are seen in Fig. 5. For unimplanted annealed Ni disks (25 mm diameter, 1.9 mm thick) the unlubricated coefficient of friction is high (>1.0) and shows erratic behavior due to stick-slip adhesion to the sliding steel ball during testing in dry $N_2$; see Fig. 5a. However for Ti + C-implanted Ni, the coefficient of friction is lower (0.75) and the frictional force does not vary greatly, implying that the adhesion has been eliminated. This effect is confirmed by examining corresponding wear tracks in Fig. 5b. The unimplanted surface is very rough and worn deeply (1.82 $\mu$m) in local areas due to adhesion and removal; it is elevated in some areas,
Figure 5. a) Friction coefficient obtained with bulk Ni disks, unimplanted and implanted with Ti and C, rotating in dry N₂ against a 1.6 mm radius 440C steel with 9 gf load (Hertzian stress: 43 MPa). b) Optical interferrometry images of unimplanted (left) and implanted (right) wear tracks.

indicating that material has been re-deposited on the surface. In contrast, the track for implanted material shows minimal wear with only shallow grooves. Thus implantation has changed the wear from adhesive to mild abrasive, which persists until the amorphous layer is worn through beyond 100 cycles in Fig. 5a. Stick-slip adhesion and wear are eliminated by hardening the surface, which deforms less during contact with the slider giving less area for adherence. In addition, the stronger implanted surface layer probably requires greater force to be torn away.

Properties of Electro-formed Ni

To assess Ti plus C implantation for Ni-based MEMS devices, we examined two alloys (Ni and Ni₈₀Fe₂₀) electro-plated during the production of LIGA components. The plating conditions and microstructure of the as-deposited metals are discussed elsewhere [15]; in both cases, fine-grained (20-600 nm) fcc material was produced. Specimens (150 µm thick) were evaluated with indentation and modeling and found to be much stronger than pure Ni (Y.S. = 1.4 and 1.9 GPa, respectively) and also harder, although the elastic modulus is not significantly changed [21,22]; see Fig. 4. The increased strength and hardness are inferred to result from the fine grain sizes.

The same implantations of Ti and C used for pure Ni produced a fully amorphous phase extending to the surface without the second, low-energy C implantation. The high fraction of amorphous phase in layer I for pure Ni (~80 vol.%) indicates that the 2x10¹⁷ C/cm², 45 keV implantation is almost sufficient for full amorphization, and we infer that defects in the electro-formed material and perhaps C impurities introduced during plating produce full amorphization. Nanoindentation and modeling of the implanted, electro-formed alloys gave mechanical properties for the amorphous phase [22] essentially the same as those deduced with pure Ni. This agreement with substrates having such different mechanical properties supports our evaluations since the amorphous phase should be same whether formed from large-grain, annealed Ni or fine-grain, electroplated Ni, and substituting 20% Fe for Ni should have minimal effect.

The critical property for ion-implanted MEMS alloys is tribological performance, and the coefficient of friction is seen in Fig 6 to be quite improved over that of unimplanted material. In this test with reciprocating sliding of a steel ball on electro-deposited Ni in laboratory ambient, the unimplanted material shows a relatively high coefficient of friction with excursions to ~1.0.
Figure 6. Friction coefficients of electroformed Ni, unimplanted and implanted with Ti + C, obtained in laboratory ambient during unidirectional, reciprocating sliding against a 1.6 mm radius 440C steel ball with 9 gf load (Hertzian stress: 43 MPa).

In contrast, that of the implanted material rises to 0.35 at 50 cycles and remains nearly constant until 350 cycles; the subsequent rise may reflect partially wearing through the amorphous layer. The large excursions in frictional force for untreated material are due to adhesion to the substrate; this behavior is again greatly reduced by implantation. It is notable that friction is lower and remains so for more cycles with implanted electroformed Ni than with implanted pure Ni (Fig. 5). This improvement is consistent with the greater hardness of electroformed Ni, although the change of atmosphere from dry N2 to lab ambient may have also reduced the friction. The harder substrate beneath the implanted layer deforms less, further reducing the contact area for adhesion to the counterface.

DIAMOND-LIKE CARBON (DLC) DEPOSITED LAYERS

There are several types of amorphous C-based materials with varying degrees of hardness due to their composition, chemical bonding and synthesis conditions. A recent review indicates the differences between these materials [3]. Materials containing H, such as those produced by chemical vapor deposition, are generally softer and may not adhere as well due to H disrupting bonds across the interface with the substrate. For H-free materials, plasma processes produce harder layers due to higher atom energies. Hardness varies with bond type: high fractions of sp3 bonds (found in crystalline diamond) produce higher hardness than do high sp2 (graphite) fractions. Methods including electron energy loss spectroscopy have been used to evaluate sp3 fraction and large values have been found (~85%) for hard, vacuum-arc deposited DLC [23]. Recent molecular dynamics simulations of the atomic structure of amorphous DLC quenched from the liquid state with a density of 3.0 g/cm³ give a somewhat lower sp3 fraction, ~65% [24]. An optimum energy has been identified for deposited atoms to produce maximum sp3 content, ~100 eV/C [3]. Details of how hard DLC forms during implantation are still under discussion. Key ideas include “subplantation”, subsurface implantation of atoms at low energy that results in accumulation and growth of sp3-bonded C due to preferred displacement of sp2-bonded C [25], and compressive stress-induced DLC formation similar to diamond at high-pressure [26]. Optimum deposition energies for high sp3 content near ~100 eV emerge from both models. The role of “thermal spikes”, melt-like zones that quench along an ion track, is not yet clear [25].

Here we evaluate hard, H-free material, known as diamond-like carbon, hard carbon, or amorphous-tetrahedral carbon (a-tC [27]). We find that vacuum-arc and pulsed-laser deposited DLC can have hardnesses approaching that of diamond. Neuville and Matthews [3] state that measuring the hardness of DLC is important to understand the material, but indentation is difficult due to substrate effects, surface effects, and deformation of the indenter tip. We show that finite-element modeling correctly accounts for these effects during nanoindentation. The dependence of sp3 content on C⁺ energy is demonstrated, and the compressive stress often found for DLC is shown to be removable by annealing without significant reduction in hardness.
Vacuum-Arc Deposited DLC

Vacuum-arc deposition was done at Lawrence Berkeley National Laboratory using methods described previously [28]. Briefly, a vacuum arc discharge is produced on a carbon cathode to generate a plasma composed largely of C⁺ ions with a directed kinetic energy of 20-30 eV. The plasma passes through a 90° magnetic filter to remove macroparticles. The substrate is pulse-biased with a duty cycles of 25%. A bias of -100V has been shown to produce high hardness DLC, but with high compressive stress, 10.5 GPa. When the bias is increased to -2 kV, the stress decreases to 2.5 GPa but the material is softer. This higher bias gives deeper penetration of C⁺ into the layer/substrate (R_p ~ 4 nm in Ni) and is used at the beginning of even the hard-layer depositions to “stitch” the layer to the substrate by intermixing their interface, with the bias subsequently being decreased to -100 V to obtain the higher hardness.

We evaluated a hard DLC layer 700 nm thick and a soft one 400 nm thick deposited on Si substrates (500 μm thick). The load vs. depth response data for both are given in Fig. 7; these layers require greater force on the indenter than used for Ni (Fig. 3) because the DLC layers are thicker and harder. The hard material shows a very elastic response, with data taken during indenter retraction falling only slightly below those taken during insertion. Accurate evaluation of DLC requires careful modeling with a sufficiently fine mesh around the contact area with elements as small as 2 nm x 20 nm for convergence of the numerical code. The diamond indenter must also be treated accurately by calibrating the rounded shape at the tip and modeling a sufficiently thick section to account for its elastic response correctly. The tip showed no indication of yielding between successive indentations and was modeled as a purely elastic solid. The compressive stress in the layers was included in the model. Values of yield stress and elastic modulus deduced from the best-fit simulations are given in Table I, and those for -100 V bias are noticeably higher than for -2 kV. Using these properties in additional simulations of hypothetical “bulk” materials gives intrinsic hardnesses of 68.4±2.5 GPa and 27.5±0.7 GPa, respectively. It is
Table I. Mechanical Properties of Diamond-Like Carbon and Diamond

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic Modulus</th>
<th>Yield Stress</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft vacuum-arc deposited DLC</td>
<td>360±10 GPa</td>
<td>14.1±0.4 GPa</td>
<td>27.5±0.7 GPa</td>
</tr>
<tr>
<td>Hard vacuum-arc deposited DLC</td>
<td>848±10 GPa</td>
<td>49.1±2.9 GPa</td>
<td>68.4±2.5 GPa</td>
</tr>
<tr>
<td>Pulsed-laser deposited DLC</td>
<td>1101±18 GPa</td>
<td>77.6±2.4 GPa</td>
<td>88.1±2.2 GPa</td>
</tr>
<tr>
<td>Diamond</td>
<td>1141 GPa</td>
<td>&gt;100 GPa*</td>
<td>~100 GPa</td>
</tr>
</tbody>
</table>

* Poisson's ratio, \( \nu = 0.100 \) used for DLC, 0.070 for diamond.

* Deduced from nanoindentation and finite-element modeling.

clear that the deposition energy greatly affects mechanical properties. High hardness is obtained for a total C+ energy of \( \approx 100 \text{ eV} + \approx 20 \text{ eV} = \approx 120 \text{ eV} \), as expected [3]. The hard DLC was evaluated previously with analytical methods developed for nanoindentation [23] and a lower bound placed on its hardness: \( \geq 60 \text{ GPa} \), in agreement with our findings. The analytical methods [29] have limited ability to evaluate thin hard layers on softer substrates for reasons stated above.

The tribological properties of vacuum-arc deposited DLC on Si have been assessed [30], and low coefficients of friction, \( \leq 0.15 \), were found. To evaluate the DLC for application to MEMS, the two layers were deposited on annealed Ni (1.9 mm thick) to \( \approx 200 \text{ nm} \) thickness. The high-stress, hard layer was partially delaminated from the Ni substrate, but the low-stress, soft layer was fully adherent. The layers were tested in the reciprocating sliding tester described above for implanted Ni. Because of the high elastic modulus of DLC, the calculated Hertzian stresses are higher, \( \approx 500 \text{ GPa} \). As seen in Fig. 8, both layers exhibited low coefficients of friction in this test, \( \approx 0.2 \), that persist for more than 1000 cycles. Notably, the softer layer performed quite well under these representative MEMS operating conditions; since it showed no signs of delamination before or after testing, it appears to be the better treatment for this application.

**Pulsed-Laser Deposited DLC**

A pulsed laser was used to deposit DLC at Sandia National Laboratories. The excimer laser (248 nm) was operated at 20 Hz repetition rate and a high energy fluence (>100 J/cm²), giving a deposition rate of \( \approx 1 \text{ Å/sec} \) on a (100) Si substrate place in the ablation plume [27]. This method produces DLC with high compressive stress, \( \approx 6-8 \text{ GPa} \). Recently, annealing methods have been identified to reduce this stress essentially to zero [31], and 2 minutes at 600°C was used for the material evaluated here. Raman and electron energy loss spectra showed only subtle changes between as-deposited and annealed DLC layers [27]. To make thick material, a layer 0.15-0.2 \( \mu \text{m} \) thick was deposited on Si (300 \( \mu \text{m} \) thick) and annealed in situ; subsequent layers were added and the structure was annealed after each to form a total thickness of 1.2 \( \mu \text{m} \) of stress-free DLC.

Representative nanoindentation response data for this layer indicate a very elastic response in Fig. 9a. The best-fit simulation is seen in Fig. 9a to fit the data well, and the fitted parameters are listed in Table I. The indenter was modeled as a purely elastic material [27] and the finite-element mesh for indentation to 160 nm depth is shown in Fig. 9b. This material has the highest yield stress of those tested and an elastic modulus that is \( \approx 90\% \) of that of diamond. Using these values for bulk material gave the intrinsic hardness versus depth curve shown in the upper part of
Fig. 9a indicating a very high hardness, 88.1 GPa, also near that of diamond. The curve is flat beyond ~50 nm depth, indicating that the indentation is sufficiently deep for plastic deformation and maximum hardness to be assessed. Due to the thickness of this layer (1.2 μm), this curve differs little from that for the DLC/Si composite, and the analytical methods developed for nanoindentation [29] correctly assess the layer hardness. However, the high elastic modulus determined by modeling is not obtained with those methods, apparently due to larger-than-expected influence of the softer Si substrate and possibly also the substantial deformation of the indenter tip [5]. Notably, the Si substrate also plastically deforms, even with this thick hard layer.

Superimposed on the deformed mesh of elements for the indenter and DLC layer in Fig. 9b is the position and shape that the diamond tip would have if it were infinitely stiff and remained undeformed. The tip is depressed by ~65 nm at the radial center of contact (left side of Fig. 9b) and a relatively abrupt change in its surface contour occurs where it contacts the DLC. These features show the importance of modeling the indenter correctly and handling it carefully. To avoid accidentally deforming the tip during testing, the specimen surface was initially located in an area where the DLC layer was absent. To verify that plastic deformation did not occur in the tip during the indentations, the tip shape was recalibrated afterwards, with no change detected. The indentation data obtained for the DLC layers are very reproducible and overlay each other. We have considered this absence of evidence for tip deformation between individual indentations [4], and with results from this very hard specimen, a lower limit can be placed on the yield strength of diamond, Y.S. > 100 GPa in compression, since stresses inside the tip are calculated...
Figure 10. Schematic showing bond conversion of C in DLC from sp\(^3\) (4-fold coordination) to sp\(^2\) (3-fold) and the resulting outward relaxation of the layer.

Figure 11. Friction coefficient of pulsed-laser deposited DLC on Si, obtained in lab ambient during unidirectional, reciprocating sliding against a 1.6 mm-radius 440C steel with 9 g\(_f\) load (Hertzian stress: ~600 MPa).

to have reached 106 GPa. The above discussions indicate how valid concerns about indentation of DLC [3] have been addressed in our work by using finite-element modeling to interpret the material response. This approach accounts for plastic and elastic deformations of the tip and substrate, allowing DLC mechanical properties to be assessed accurately. Preliminary work indicates that the same yield strength and modulus are obtained with layers as thin as 50 nm [32].

The elimination of compressive stress allows DLC layers to be more widely used and appears not to reduce their hardness significantly. An atomic model has been developed to explain the stress reduction based on conversion of some C atoms from sp\(^3\) to sp\(^2\) bonding [31], as indicated schematically in Fig. 10. This conversion is supported by several observations occurring during annealing: increased optical absorption, reduced atomic density, increased conductivity, and conversion of the layer to nanocrystalline graphite at 800° C [33]. This bonding change actually increases the atomic volume of the C atom, just as the atomic density of graphite is lower than that of diamond. However, the sp\(^2\) atomic volume is not equiaxed, but is extended in one direction, as indicated in Fig. 10. In a compressive layer, this direction is energetically preferred to align normal to the layer, which can then relax outward for a net reduction in stress. For an initial stress of ~7 GPa, 6% of the C atoms are required to transform to completely relieve stress; using the lower value of 65% for the initial sp\(^3\) content, the number of sp\(^3\) atoms in the layer would then decrease by only ~1/10, consistent with the very high remaining hardness determined here. Such annealing should relieve stress in DLC layers produced by other methods also.

The viability of pulsed-laser deposited, annealed DLC layers as tribological coatings was examined for a 0.17 \(\mu m\) layer on Si with the above same reciprocating sliding conditions. The friction coefficient is seen in Fig. 11 to be low, ~0.2, but decreasing slightly with continuing sliding. This decrease possibly represents a change on the DLC surface from sp\(^3\) to sp\(^2\) bonds and a graphitic surface during sliding contact. Further testing is needed to determine if the coefficient of friction will stabilize at a low level after a greater number of cycles, like those seen in Fig. 8. To verify the applicability of this material to Ni-based MEMS, the effects of the stress-relieving anneal on the fine-grained microstructure of electroformed Ni need to be assessed. It is also possible that thin (\(< 0.1 \mu m\)) as-deposited layers give extended benefits without annealing.
DISCUSSION

The amorphous phases examined here show exceptional properties compared to their crystalline counterparts. Amorphous Ni(Ti,C) is harder than bearing steel and other hard amorphous metals of Ni or Fe. Approximately 20 at.% each of Ti and C are required for its formation, which can be achieved by adjusting ion energies and fluences to produce overlapping profiles with appropriate concentrations. The increased hardness gives a reduced contact area on the surface during sliding contact, resulting in much less adhesion and a change to mild abrasive wear. We have also examined amorphous Fe(Ti,C) produced by pulsed laser deposition and find very similar hardness\[20\]. It is reasonable to predict that steels implanted with Ti and C are similarly hardened, and that this hardness contributes to the reduced friction and wear observed for them \[8,9,11\]. Such hardening probably contributes to the improved tribological performance observed for Co alloys \[10\] as well.

The hardness of DLC can approach that of crystalline diamond, the hardest known substance. This is achieved by adjusting deposited ion energies to near ~100 eV. The plasma energy is not known for pulsed-laser deposition, but the very hard DLC layer examined here (88 GPa) was produced with high laser fluences, which presumably give higher deposition energies perhaps approaching the optimum value. With vacuum-arc deposition, such energies occur only when the pulsed bias is on, ~25% of the time, which could account for the lesser hardness (68 GPa) of its DLC at 100V bias. Increasing the bias to 2 kV significantly reduced the hardness.

Both materials provide low coefficients of friction for electroformed Ni used for MEMS components. Ion implantation matches key requirements for such a treatment: it is done at room temperature, produces no dimensional change, and the layer does not have an abrupt interface with the substrate thus insuring good adherence. Moreover, the resistance of the implanted layer to electropolishing observed during our TEM specimen preparation implies that the surface may be corrosion resistant. The small areas of miniature components should allow implantation at lower cost than for macroscopic components currently being commercially treated.

Deposition of DLC is also done at room temperature, and good performance is obtained with thicknesses (~0.2 μm) that perturb component tolerances only minimally. We are currently investigating the tribological performance of even thinner layers (<0.1 μm). Layer adherence is good with higher-energy ions that intermix the interface and produce less compressive stress. Thin (~20 nm) DLC layers are already applied commercially as protective coatings for computer disk drives to prevent damage when the head contacts the spinning platter. In addition, DLC layers are smooth and pin-hole free at ~10 nm thickness, and their chemical inertness is expected to inhibit corrosion. The anneal treatments identified to reduce compressive stress \[30\] can be expected to broaden the applicability of DLC coatings.

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