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Diamond-Like Nanocomposite Coatings for LIGA-Fabricated Nickel Alloy Parts

T.W. Scharf and S.V. Prasad

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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T.W. Scharf and S. V. Prasad

Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0889

Abstract

A commercial plasma enhanced chemical vapor deposition (PECVD) technique with planetary substrate rotation was used to apply a thin (200-400 nm thick) conformal diamond-like carbon (DLC) coating (known as a diamond-like nanocomposite (DLN)) on LIGA fabricated Ni-Mn alloy parts. The PECVD technique is known to overcome the drawbacks associated with the line-of-sight nature of physical vapor deposition (PVD) and substrate heating inherent with traditional chemical vapor deposition (CVD). The purpose of the present study is to characterize the coverage, adhesion, and tribological (friction and wear) behavior of DLN coatings applied to planar and sidewall surfaces of small featured LIGA Ni-Mn fabricated parts, e.g. 280 μm thick sidewalls. Friction and wear tests were performed in dry nitrogen, dry air, and air with 50% RH at Hertzian contact pressures ranging from 0.3 to 0.6 GPa. The friction coefficient of bare Ni-Mn alloy was determined to be 0.9. In contrast, low friction coefficients (~0.02 in dry nitrogen and ~0.2 in 50% RH air) and minimal amount of wear were exhibited for the DLN coated LIGA Ni-Mn alloy parts and test coupons. This behavior was due to the ability of the coating to transfer to the rubbing counterface providing low interfacial shear at the sliding contact; resultantly, coating one surface was adequate for low friction and wear. In addition, a 30 nm thick titanium bond layer was determined to be necessary for good adhesion of DLN coating to Ni-Mn alloy substrates. Raman spectroscopy and cross-sectional SEM with energy dispersive x-ray analysis revealed that the DLN coatings deposited by the PECVD with planetary substrate rotation covered both the planar and sidewall surfaces of LIGA fabricated parts, as well as narrow holes of 300 μm (0.012") diameter.

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1. Introduction

Deep X-ray lithography based techniques such as LIGA (German acronym representing Lithographie, Galvanoformung and Abformung, or Lithography, Electroforming, Molding) are now well established to fabricate net shape components for high aspect ratio microsystems (HARMS) [1,2]. Unlike other microfabrication techniques, LIGA lends itself to a broad range of materials including metals and alloys. Currently, the LIGA fabricated Ni-Mn alloy parts are being considered in newer designs of nuclear safety devices. While Ni-Mn alloys may meet many of the structural and mechanical (yield and tensile strength) requirements for these intended applications, their tribological (friction and wear) behavior remains suspect. For instance, the high friction coefficient of pure Ni in the absence of external fluid film lubrication (μ = 0.6 –1.2), and its stick-slip behavior could potentially interfere with the performance and reliability of the moving mechanical assembly [2]. Surface treatments and coatings to reduce friction between contacting sliding surfaces are therefore essential to ensure reliable operation.

In conventional stronglink safety devices, molybdenum disulfide (MoS_2)-based solid lubricant coatings (e.g., Molykote, Vespel and Electrofilm) are used to mitigate the friction and wear problems [2]. Molybdenum disulfide belongs to the family of transition metal dichalcogenides that are well-known for their solid lubricating behavior in dry environments. However, they oxidize in environments containing water vapor and oxygen, and thereby lose their lubricating behavior. Since the conventional devices are hermetically sealed with dry nitrogen, oxidation of the MoS_2 solid lubricant is not a major concern. The newer devices, based in part on LIGA technology, are intended to function in atmospheres without the hermetic seal. Thus, there is need to develop friction-reducing coatings and surface treatments that are effective in both dry and humid environments. To this end, we have examined the feasibility of applying diamond-like carbon (DLC) coatings on LIGA fabricated Ni-Mn alloy parts that will effectively reduce the friction coefficients to below 0.2 in dry and humid environments.

The DLC family of coatings is known to exhibit an unusual combination of tribological and mechanical properties: low friction coefficients and low wear rates in dry and ambient air, relatively high hardness, and high elastic modulus [3,4]. However, the ability of DLC family of coatings to lubricate parts in pressure regimes relevant to microsystems operation is not well understood. Secondly, the application of these coatings at length scales relevant to LIGA Microsystems is a major challenge. The miniature nature of LIGA MEMS parts--several hundred microns to millimeters in size--poses a tough challenge to coating technology. Handling of individual LIGA MEMS elements is extremely difficult, and such techniques as resin bonding and burnishing that are commonly used for coating parts in conventional devices can be ruled out. Physical vapor deposition (PVD) techniques (e.g., sputtering, ion beam deposition, evaporation, etc.) are typically line-of-sight processes, whereas the coating is most needed on the sidewalls. Unlike PVD, chemical vapor deposition (CVD) is a non-line-of-sight technique that can deposit conformal coatings. However, CVD is a high temperature process, and subjecting the Ni-Mn alloy parts to CVD processing temperatures will result in grain growth and Hall-Petch softening. Thus, we have opted for plasma enhanced chemical vapor deposition (PECVD) technique which has the potential for conformally coating entire LIGA parts without having to raise the substrate temperatures. The PECVD is a process in which the constituents of the vapor phase react to form a solid film assisted by an electric discharge. In the PECVD technique, the gas molecules are mainly dissociated by electron impact generating neutral, radical, and ion species [5]. These species arrive on a surface and react with each other in the coating forming process. Since the gas molecules are activated by the energetic electrons instead of thermal energy, the reaction temperature can be easily reduced. Thus, coatings can be deposited at temperatures typically less than 200°C, since the activation energy for the chemical reaction is provided by the glow discharge on the biased substrate. The ability of PECVD to deposit coatings at much lower temperatures than conventional CVD prevents any potential microstructural changes and mechanical property degradation of the base Ni-Mn alloy part. In this particular study, we have selected a diamond-like nanocomposite (DLN) coating that can be applied by PECVD from siloxane vapors which contain Si and O in addition to C and H species. The microstructure of DLN coatings is comprised of a diamond-like network of amorphous C:H and a second glass-like network of Si:O with minimal bonding between the two networks [6,7]. Bekaert Advanced Coatings Technologies has developed a commercial process for depositing DLN coatings which are known by their trade name, Dylyn™. This report describes the results of our study on the tribological behavior of DLN (Dylyn™) coatings in environments and load regimes relevant to the future generation nuclear safety devices, adhesion of DLN to Ni-Mn alloy substrates, and our initial efforts to apply these coatings onto LIGA fabricated parts.

2. Experimental Conditions

The DLN coatings were deposited by a PECVD process from a commercial vendor, Bekaert Advanced Coating Technologies [7]. The plasma is formed from a siloxane precursor using a hot filament, and ionized species are deposited onto negatively biased substrates. Although there was no deliberate substrate heating during deposition, however, local temperatures can rise up to a maximum of 200°C due to ion impingement on the surface according to Bekaert Advanced Coating Technologies. We have applied the standard commercial process to deposit the DLN coatings on planar test coupons. Previous studies [2] revealed that the standard commercial process was inadequate to conformally coat the more complicated LIGA fabricated parts. The process was subsequently modified by incorporating planetary substrate rotation to obtain the diamond-like structure on the sidewalls of LIGA parts. We have also devised a novel strategy to successfully overcome the handling issues associated with coating miniature parts.

Tribological tests were performed on 200 nm thick DLN coatings deposited on silicon and LIGA Ni-Mn substrates. Silicon wafers were chosen to minimize the surface topographical effects, and substrate-coating adhesion on friction. There is also prior published data on the tribology of DLN coatings on silicon wafers for comparison with current measurements [8-10]. In addition, we wanted to first ensure that the tribological properties of the coatings that we are getting from Bekaert Advanced Coating Technologies were reproducible before we applied them on real parts made from precious LIGA Ni-Mn alloys. After these preliminary tests, the coatings were deposited on Ni-Mn moats (byproducts from LIGA electrical contact spring processing) to assess the adhesion of DLN coatings to Ni-Mn alloys, and to evaluate the coverage on the sidewalls, including the inner walls of 300 μm diameter holes drilled on the sidewalls of moats (280 μm thick). Subsequent studies revealed that a 30 nm thick Ti interlayer was necessary for improved adhesion of DLN to Ni-Mn alloys.

Friction measurements were made on planar surfaces using a ball-on-disk linear wear tester (Fig. 1a). The tests were performed in unidirectional sliding mode. The wear tester has the capability to evaluate the friction characteristics in specific locations down to approximately 1 mm track lengths. The tester was housed in an environmental chamber shown in Fig. 1b. Oxygen content in the chamber was measured using a Delta F Platinum Series oxygen monitor, and the humidity was monitored by measuring the dew point. Tests were conducted in dry nitrogen (<1% RH, <10 ppm O_2 and <100 ppm H_2O), dry air (<1% RH), and ambient air (~50% RH) environments using a 3.175 mm diameter

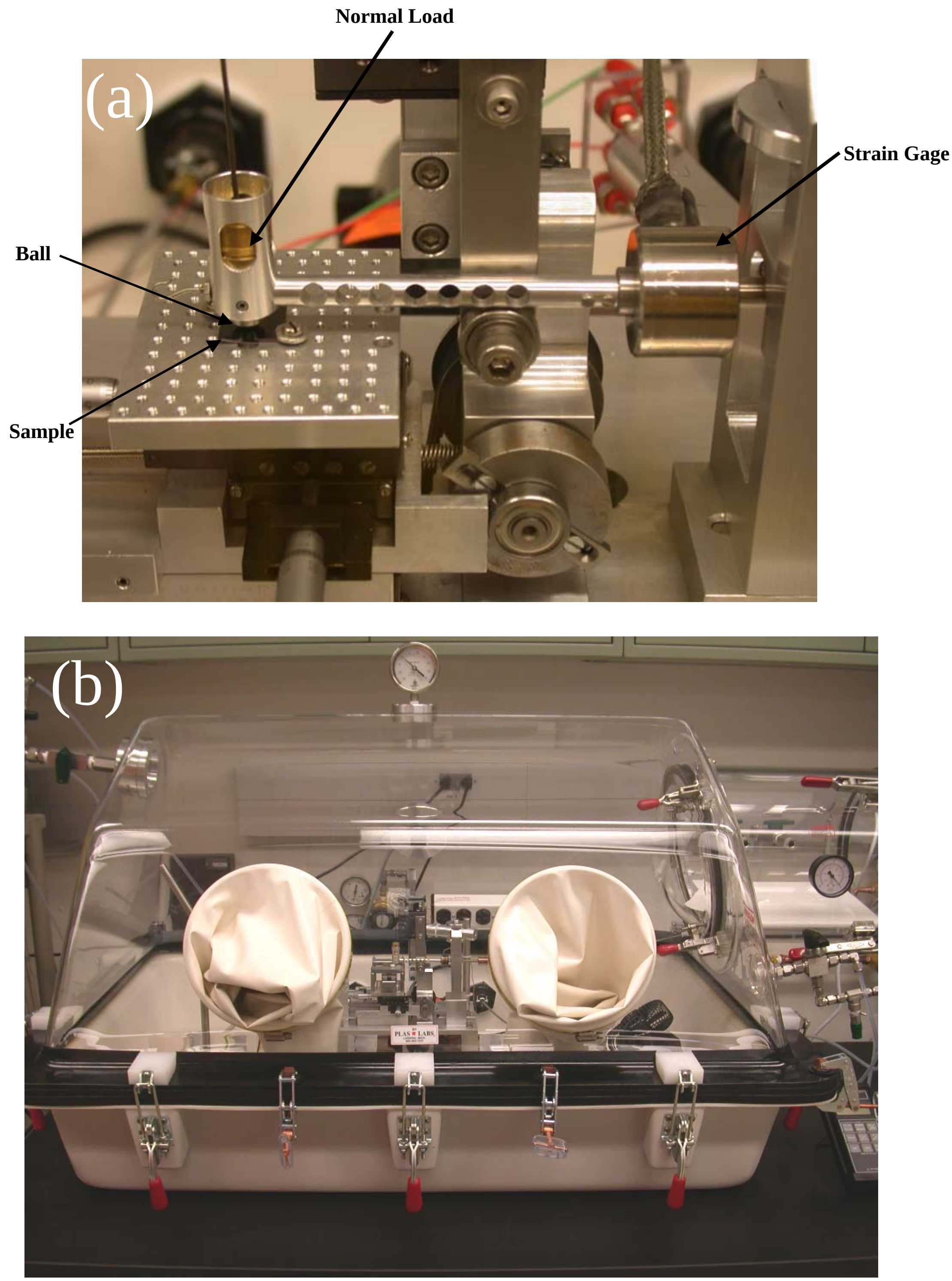


Figure 1. Photographs of (a) the linear friction and wear tester, and (b) the environmental chamber housing the tester.

Si_3N_4 ball (Hoover Precision Products) at normal loads of 98, 245, or 490 mN. These loads correspond to initial mean Hertzian contact stresses of ~0.3, 0.4, and 0.6 GPa, respectively. A 500mN transducer (Sensotec) in the load arm measured the tangential load over a track distance of 1 to 3 mm, which was dependent on the size of the test coupon. The sliding speed was 3.3 mm/s. The ratio of tangential to normal load is the coefficient of friction (COF). Friction and wear tests were run for either 1000 or 2000 unidirectional cycles.

After the sliding tests, the counterfaces were separated and the wear tracks and transfer films on the balls were analyzed by optical microscopy, Raman spectroscopy, and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) capable of recording X-ray dot maps. Raman spectra were obtained using 514-nm argon laser excitation at a low power of 20 mW. The laser beam was focused to a ~1 μm spot size. At this laser power density (~25 mW/μm^2), no changes in the spectra due to surface heating could be seen. The acquisition times were 60 seconds/spectrum with 5 total accumulations taken to average each spectrum. Raman shifts were measured over a frequency range from 200 to 1800 cm^{-1}, with 1 cm^{-1} resolution. In addition, focused ion beam (FIB) microscopy was used to prepare cross-sections from the sidewalls of DLN coated parts suitable for SEM.

3. Tribological Measurements

3.1 Friction and Wear Behavior of Bare LIGA Ni-Mn Alloys

Typical friction traces of a silicon nitride ball sliding against uncoated Ni-Mn substrate (LIGA moat) at normal loads of 98 and 490 mN in air (50% RH) and dry nitrogen (<1% RH) are shown in Fig. 2. The averaged coefficients of friction (COF) are 0.55 and 0.9 at normal loads of 98 and 490 mN, respectively. It should also be noted that the friction coefficients of Ni-Mn alloys were the same in all the three environments. The high COF and large fluctuations in friction force imply that the tribological behavior of LIGA Ni-Mn is typical of metallic contacts [2,11]. Furthermore, Fig. 2 shows that at the higher normal load, the COF increased in both environments. Once the adsorbed surface layers and native oxide films are removed, the softer Ni-Mn surface begins to deform plastically as shown by the secondary electron image inside the wear track (Fig. 3) generated with a 490 mN load in 50% RH air. The topography of the wear scar is extremely rough and there is a significant amount of grooves in the wear scar. In a previous study, it was observed that steel balls rubbing against a LIGA Ni coupon in dry

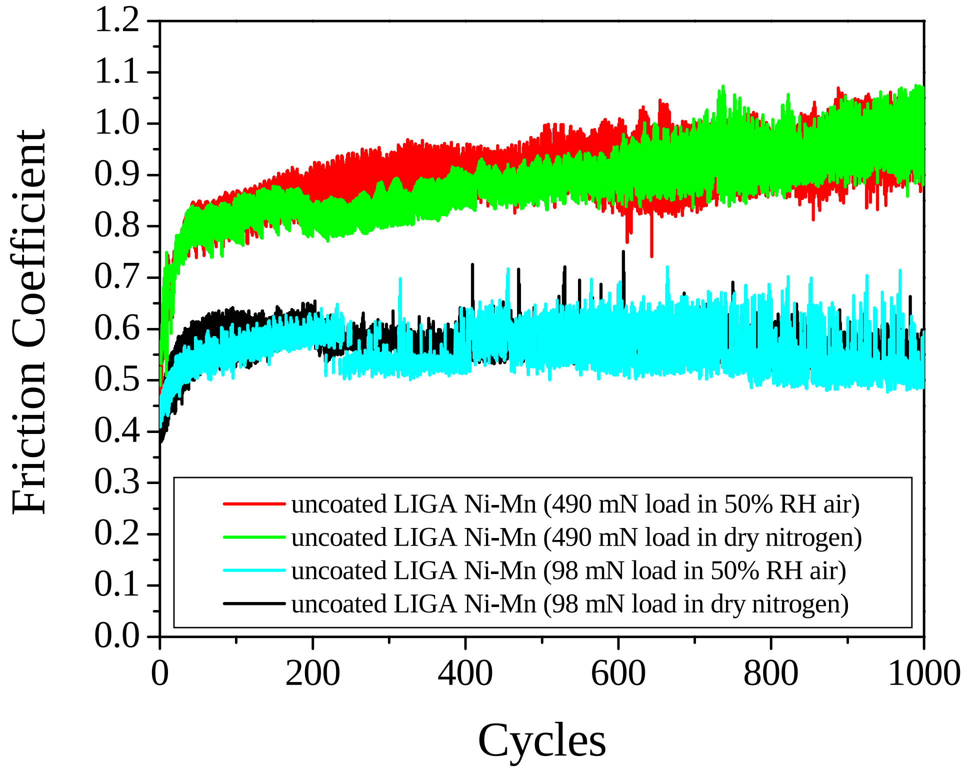


Figure 2. Typical friction behavior of uncoated LIGA Ni-Mn surface against a silicon nitride ball in dry nitrogen and humid air environments, and under 98 and 490 mN normal loads.

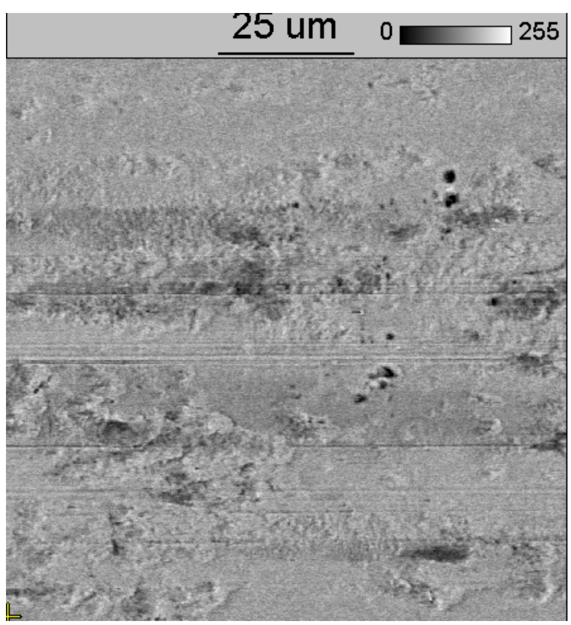


Figure 3. SEM secondary electron image of the wear track of uncoated Ni-Mn showing severe plastic deformation. Test was at 490 mN load after 1000 sliding cycles in 50% RH air.

nitrogen environments exhibited a similar COF and plastic deformation inside the track [2]. This plastic deformation could potentially interfere with the performance and reliability of microsystems. Since the relative maturity of Ni and Ni alloy processing make them the materials of choice for LIGA microsystems, coatings to mitigate this type of wear behavior are therefore essential.

3.2 Friction and Wear Behavior of DLN on Silicon

Tribological measurements were first made on 200 nm thick diamond-like nanocomposite coatings deposited on silicon (100) wafers. The objective of this set of measurements was to evaluate the friction behavior of the coatings in load and environments relevant to a LIGA maturation program. Fig. 4 shows averaged COF of a DLN coating against a Si_3N_4 ball at a normal load of 490 mN in 50% RH air, <1% RH dry air, and <1% RH dry nitrogen environments. In both dry nitrogen and dry air, the DLN coatings exhibited very low friction (COF ~0.02 in dry nitrogen, COF ~0.05 in dry air). Adding humidity (water content) in the environmental chamber resulted in higher friction behavior, i.e., COF ~0.2 to 0.23, but still much less than that of bare Ni-Mn alloy tested under identical conditions. The COF values of DLN coatings on silicon substrates in dry nitrogen [2] and dry air [8] environments are in agreement with previously published reports. Specifically, COF values of ~0.05 were observed for the same coating in dry air (~3% RH) using both reciprocating sliding [8] and pin on disk [9] tests. However, in these reports [8,9] COF values of ~0.05 were determined in ambient air (~30 to 60% RH) environments which do not agree with our measurements at 50% RH. The major differences between the current measurements and the literature are that the published data was generated in lab air, which does not have a measure and control of all the species present during testing, as opposed to our environmental chamber where there is stricter control on the environment, e.g. water vapor, and the initial mean Hertzian contact stresses were slightly higher than ours, e.g. 0.7 GPa and higher.

High resolution scanning electron microscopy (HRSEM) of the wear track (Fig. 5a) on DLN coated Si revealed practically no signs of wear or debris generation in dry nitrogen, unlike the wear track on bare Ni-Mn surface (Fig. 3a). Examination of the Si_3N_4 ball after the friction test revealed a smooth adherent transfer film on the otherwise pitted nitride ball (Fig. 5b). Energy dispersive X-ray analysis showed the transfer film was too thin to analyze the major elements from the coating: carbon, silicon, and oxygen. Thus, the more surface sensitive Raman spectroscopy technique was used to determine the chemical constituents of the transfer film on the ball surface. The spectrum shown in

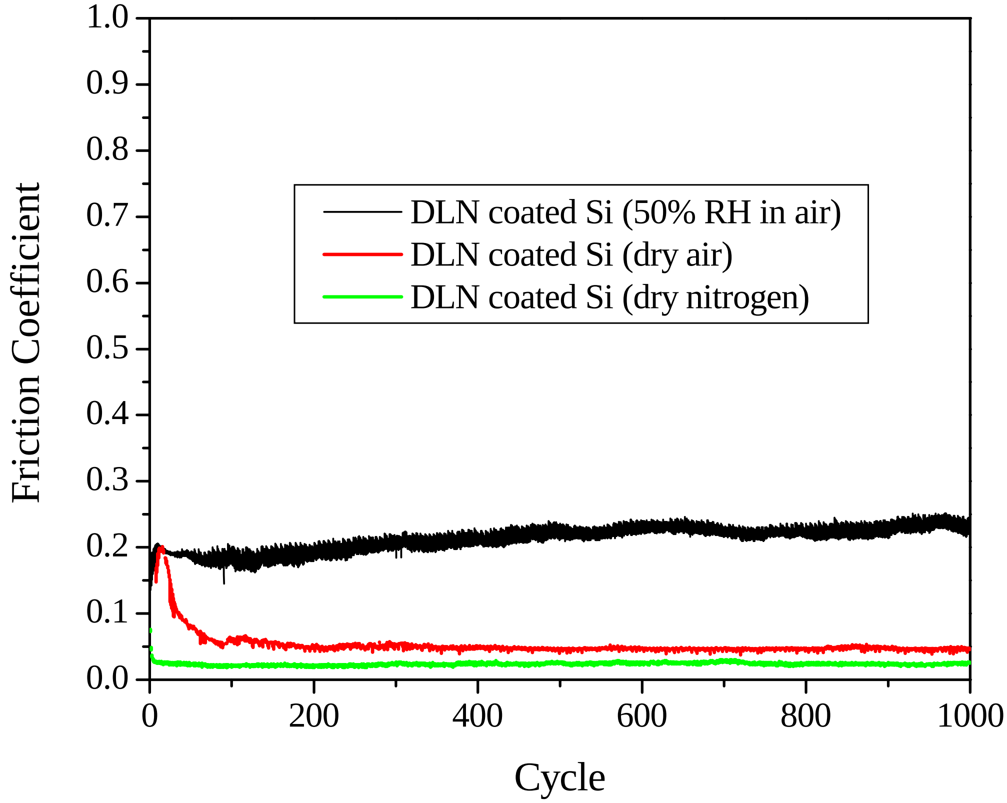


Figure 4. Typical friction behavior of DLN coating against a silicon nitride ball at a normal load of 490 mN in 50% RH air, <1% RH dry air, and <1% RH dry nitrogen environments.

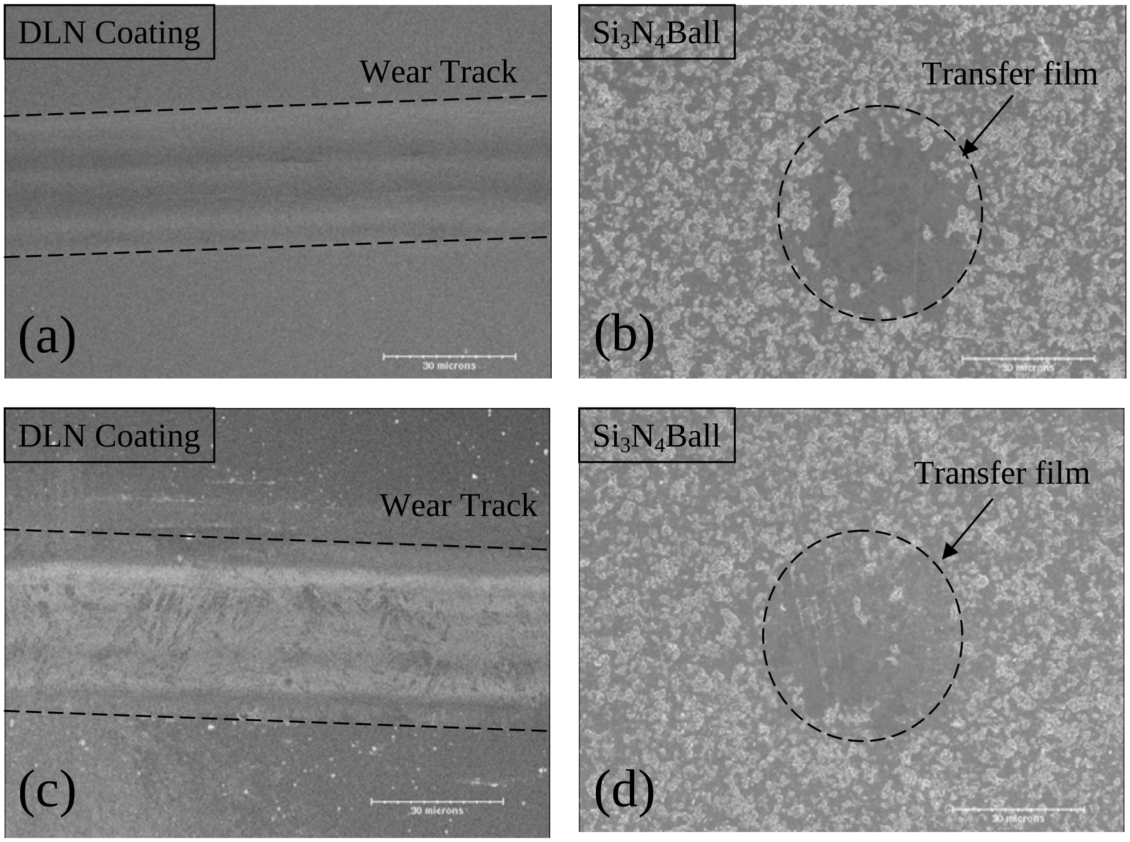


Figure 5. SEM secondary electron images of (a) wear track on DLN coated Ni-Mn, and (b) transfer film on silicon nitride ball in dry nitrogen; (c) wear track on DLN coated Ni-Mn, and (d) transfer film on silicon nitride ball in 50% RH air.

Fig. 6 indicated that a graphitic form of carbon (D and G peaks) was present on the ball as a result of rubbing on the DLN coating; a spectrum of a non-rubbed area of the ball shows peaks representative of Si_3N_4. Graphitic carbon is the thermodynamically stable phase that could result from thermal or frictional modification of other forms of carbon [3,10]. HRSEM images inside the wear track and on the transfer film after testing in 50% RH air are shown in Fig. 5c and 5d, respectively. Similar EDS and Raman results compared to the dry nitrogen test are exhibited for the transfer film on ball surface, although the wear track appears to be more plastically deformed in 50% RH air.

The steady state COF traces shown are a result of interfacial sliding between the DLN coating on the silicon test coupon and the transfer film of DLN that came off the coating and adhered to the Si_3N_4 ball. The initial run-in during the first 50 cycles in Fig. 4 for dry testing environments represents the regime where the tribological contact is between the DLN coating and the bare Si_3N_4 ball, and once a transfer film of sufficient thickness is built up, the COF is reduced to a steady state value of 0.02 to 0.05. Past tribological research on DLN coatings confirmed the presence of third bodies (e.g., transfer films) in the sliding contact, which were also determined to control the COF and wear rates in dry and ambient air environments [2-4,8-10].

3.3 DLN Adhesion to Ni-Mn Substrates

The DLC family of coatings is not known to have good adhesion with substrates that do not contain any carbide forming elements. Since nickel is not a carbide forming element, we have applied a thin titanium adhesion layer (well known carbide former), prior to depositing DLN films on Ni-Mn alloys. To this end, we have performed linear wear tests to evaluate the adhesion with and without a Ti bond layer (~30 nm thick) grown on Ni-Mn coupons. Fig. 7 shows COF traces of DLN coatings on Ni-Mn alloy coupons with and without the Ti bond layer; a typical friction trace on uncoated Ni-Mn alloy is shown for comparison. Friction measurements were made at a normal load of 490 mN (0.8 GPa maximum initial Hertzian contact stress) in ~50% RH air. The COF of bare Ni-Mn is very high (~0.9) for the duration of the test, which was also observed in Fig. 2 for the uncoated Ni-Mn moat. A significant lowering in the COF (~0.1 to 0.16) is exhibited with both DLN coatings with and without the Ti bond layer, similar to the COF of DLN on Si substrate, previously shown in Fig. 4 at 50%RH in air. The friction behavior of the DLN coatings indicated that both coatings remained adhered to the substrates regardless of the Ti bond layer, since there were no major differences in the friction behavior. However, SEM analyses of wear scars revealed that this was not the

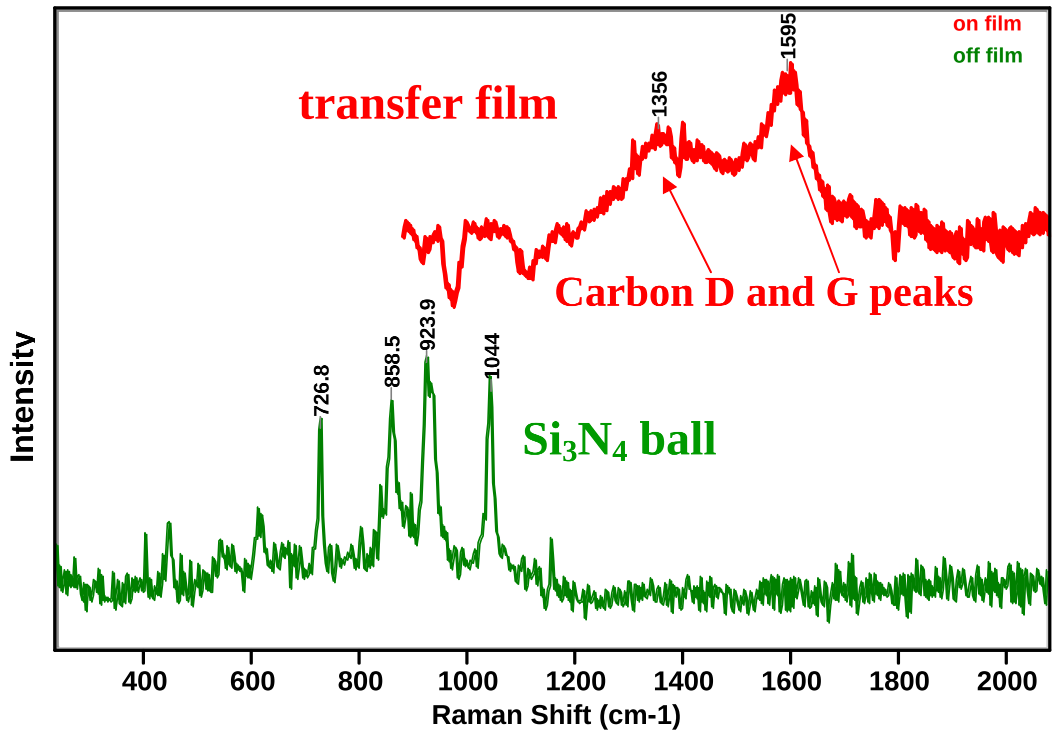


Figure 6. Micro Raman spectrum of a transfer film on a silicon nitride ball after sliding against a DLN coating. A spectrum from bare silicon nitride ball (unworn) is shown for comparison.

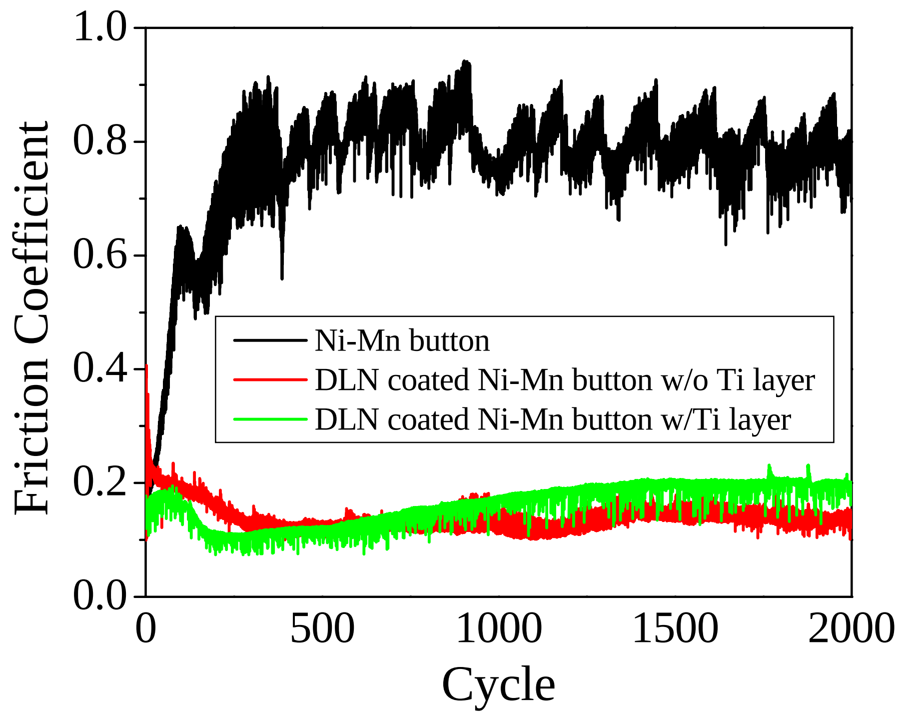


Figure 7. Typical friction behavior of DLN coatings on Ni-Mn coupons with and without a Ti bond layer; a typical friction trace on uncoated Ni-Mn alloy is shown for comparison. Measurements were made at a normal load of 490 mN (0.8 GPa maximum Hertzian contact stress) in ~50% RH air.

case. Figs. 8a (low magnification) and 8b (high magnification) show secondary electron images of the wear scars on DLN coated Ni-Mn coupon without the Ti bond layer. The images show a heavily worn area inside the track suggesting the coating delaminated from the underlying Ni-Mn coupon. Indeed, EDS X-ray dot maps showed the coating was worn away inside the wear track exposing the underlying Ni-Mn. The carbon Kα X-rays shown in blue in Fig. 8c show more intense areas outside the wear track (i.e., coating) than inside the wear track with the exception of some carbon patches scattered throughout the wear track. EDS analysis in point mode confirmed that these patches were richer in carbon, silicon, and oxygen than the underlying Ni-Mn. The Ni Kα X-rays shown in green in Fig. 8d clearly confirm almost pure Ni areas inside the wear track revealing the coating delaminated, thus exposing the Ni-Mn. Furthermore, there were no Si peaks inside the Ni-Mn wear tracks suggesting that the Si from the carbon-rich transferal patches inside the track were from the coating.

An SEM micrograph of the transfer film on the Si_3N_4 ball is shown in Fig. 9. Three EDS spectra were collected in the areas depicted in Fig. 9. Area 1 showed small amounts of carbon and oxygen from the transfer film and nickel from the substrate, which most likely transferred to the ball after the coating delaminated. Area 2 is too thin to detect any X-rays from the carbon or oxygen from the coating, and nickel from the substrate. More surface sensitive techniques like the previously shown Raman spectroscopy need to be used to determine the chemical constituents present. Area 3 shows background silicon and nitrogen X-rays representative of the unworn Si_3N_4 ball. In summary, the low friction observed without the Ti bond layer is due to transferal of DLN coating material spread throughout the wear track during sliding, despite the delamination of the DLN coating. In other words, interfacial sliding between the transfer film on the ball and the detached coating material re-circulated in the wear track is responsible for the low friction although this is not a favorable friction/wear mechanism for longer duration sliding.

In contrast, the DLN coatings with the Ti bond layer showed no signs of delamination under the exact same sliding conditions. Fig. 10a shows a low magnification SEM micrograph of multiple wear tracks on the DLN coating. A higher magnification SEM image of the wear track is shown in Fig. 10b; clearly there is less wear than the DLN coating without the Ti bond layer. Dark patches of material can also be seen inside the wear track suggesting material came off the transfer film on the ball to the coating. EDS spot analysis in Fig. 10c revealed the presence of carbon and silicon inside and outside the wear track with equal intensities confirming the coating did not delaminate. The underlying nickel peak from the substrate is slightly higher in intensity

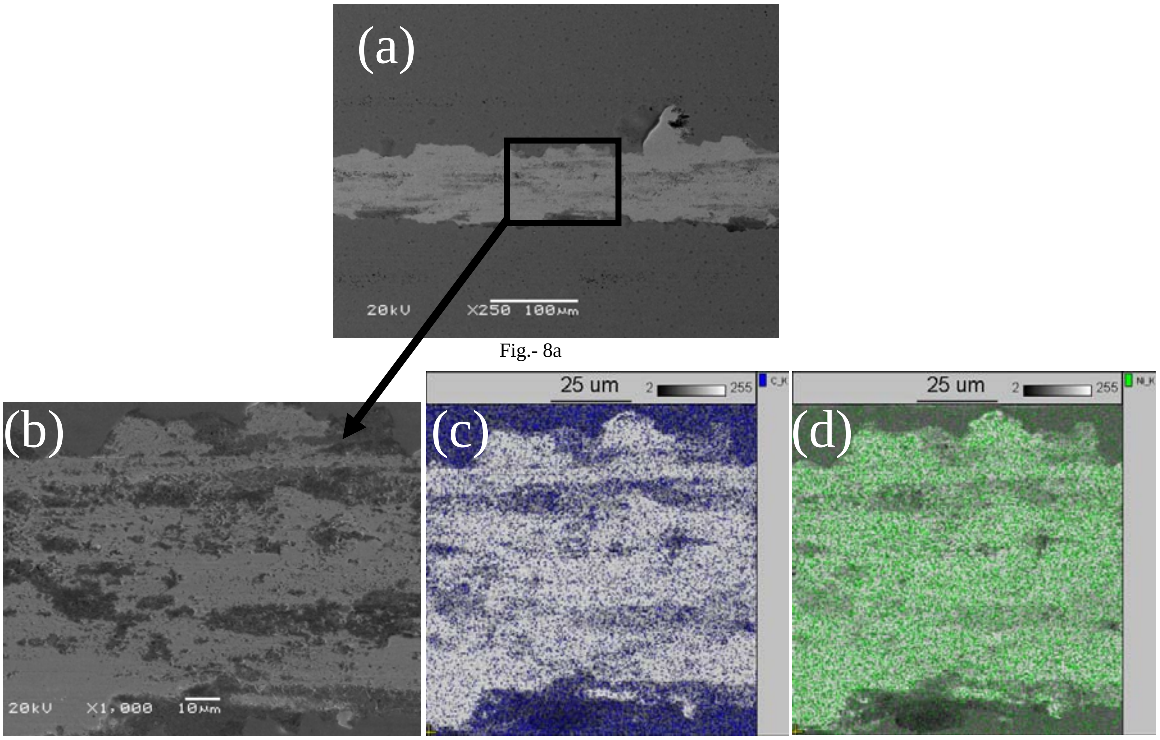


Figure 8. SEM secondary electron images of a wear track on DLN coated Ni-Mn coupon without the Ti bond layer (a and b). X-ray dot maps inside the wear track displaying the presence of (c) C Kα and (d) Ni Kα X-rays.

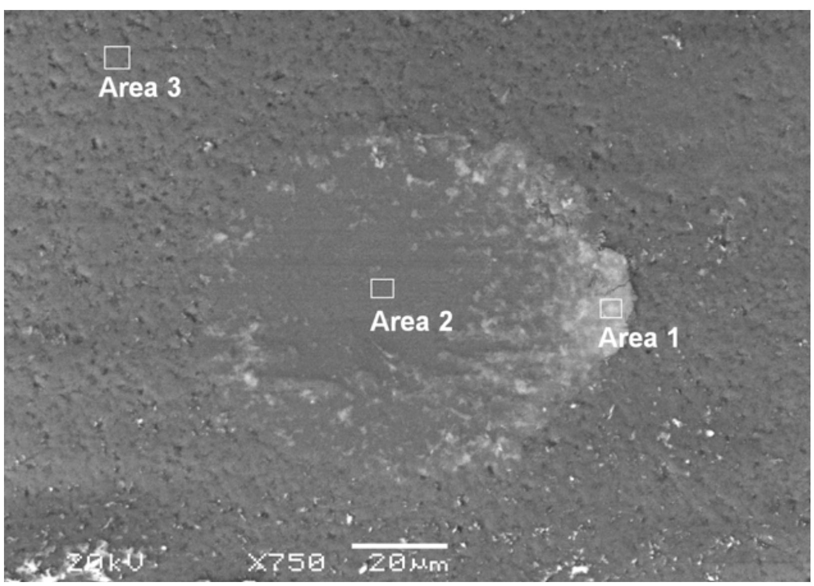


Figure 9. SEM secondary electron image of a transfer film on a silicon nitride ball after sliding on a DLN coated Ni-Mn coupon without the Ti bond layer in ~50% RH air. Three EDS measurements were taken in the areas depicted (see text for more details).

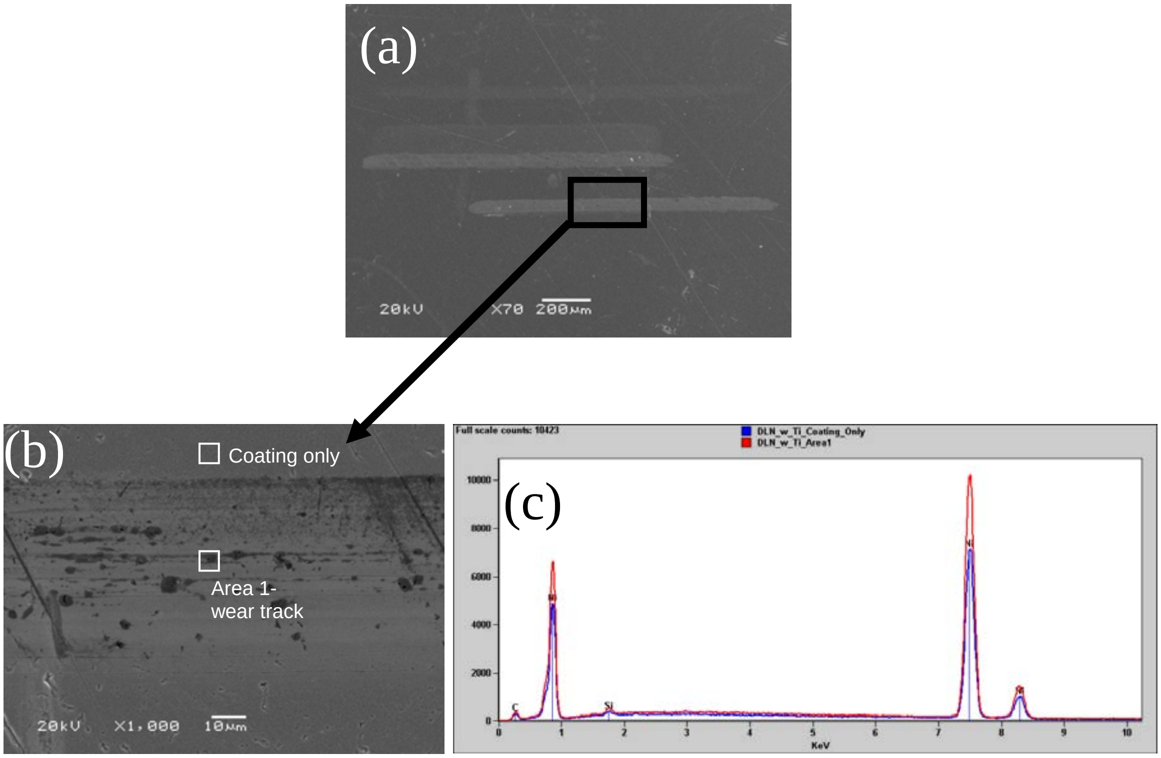


Figure 10. SEM secondary electron images of a wear track on DLN coated Ni-Mn coupon with the Ti bond layer (a and b). EDS spot analysis (c) in two areas shown in (b) revealed the presence of carbon and silicon inside and outside the wear track with equal intensities confirming the coating did not delaminate.

inside the wear track compared to the unworn coating suggesting some wear has taken place. Fig. 11 shows an SEM image of the transfer film on the Si_3N_4 ball. Area 2 shows a carbon rich patch with a small amount of oxygen, and area 1 is too thin to detect any carbon or oxygen. Neither of the areas show nickel from the underlying substrate, which was previously determined to transfer to the ball when the DLN coating without the Ti bond layer delaminated. In conclusion, poor adhesion of DLN to Ni-Mn alloy substrates is observed without a bond layer, and thus a thin Ti (carbide former) interlayer is necessary for improved adhesion.

3.4 DLN Coatings on the Sidewalls of Ni-Mn Alloy Substrates (Moats):

For many applications, the coating is most needed on the sidewalls. In order to evaluate the coverage and tribological behavior of the DLN coating on the sidewalls, large size Ni-Mn moats were coated. Fig. 12 shows friction traces for Si_3N_4 balls sliding on the sidewalls of DLN coated Ni-Mn moats at normal loads of 98 and 490 mN in air (50% RH). The DLN coating steady-state coefficients of friction decreased with increasing contact stress, ~0.14 and ~0.09 at 98 and 490 mN loads, respectively, and are significantly less than that of the uncoated Ni-Mn moat (again shown for reference). This trend of decreasing COF with increasing contact stress, opposite of uncoated Ni-Mn, has been observed for DLC and DLN coatings, consistent with the friction behavior in a Hertzian contact, $COF=s/p_m$, where s is an interfacial shear strength and p_m is the elastic contact stress [12]. In addition, a friction trace is shown in Fig. 12 for a DLN coated Si_3N_4 ball sliding against a DLN coated Ni-Mn moat. This self-mated contact does not show any improvement in COF in comparison to the bare Si_3N_4 ball sliding against the DLN coated Ni-Mn. Thus, coating one of the rubbing surfaces is adequate for improved tribological behavior. In contrast, self-mated contacts for some DLC (nearly frictionless carbon) [13,14] and diamond (ultrananocrystalline diamond, UNCD) [15] coatings have shown friction reductions in ambient air. For example, the COF was substantially higher for a Si_3N_4 ball sliding on UNCD coatings (UNCD wears and abrades the Si_3N_4 ball) than for self-mated contacts. Under any ambient conditions, UNCD rubbing against itself exhibits very low COF since water is an effective interfacial lubricant on the already passivated coating. In contrast, the moisture present in the atmosphere for DLN self-mated contacts is responsible for the higher friction since it is speculated the mixed carbon sp^2 (graphitic) to sp^3 (diamond) bonding is not fully passivated of dangling bonds [3,4]. In summary, DLN transfers to the counterface easily and thus self-mated contacts are not necessary for improved tribological behavior of coated LIGA Ni-Mn parts.

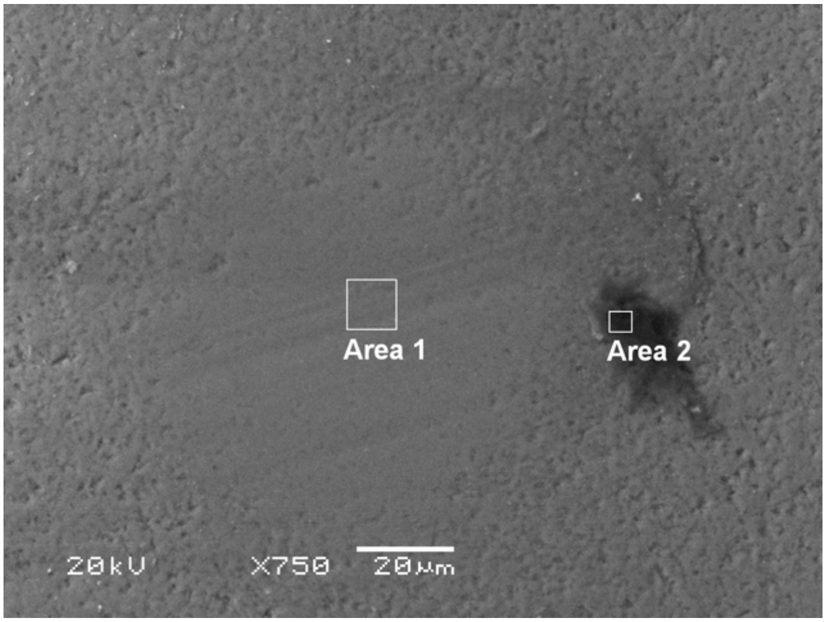


Figure 11. SEM secondary electron image of a transfer film on a silicon nitride ball after sliding on a DLN coated Ni-Mn coupon with the Ti bond layer in ~50% RH air. Two EDS measurements were taken in the areas depicted (see text for more details).

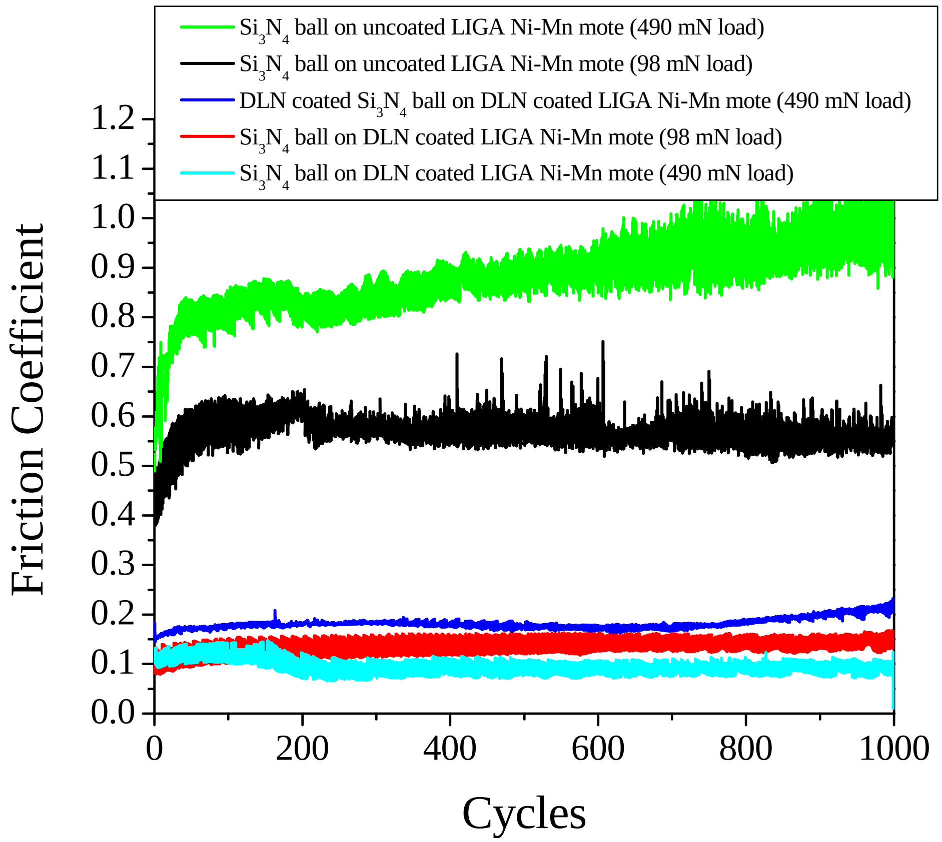


Figure 12. Typical friction behavior of silicon nitride balls sliding on the sidewalls of DLN coated LIGA Ni-Mn moats at normal loads of 98 and 490 mN in air (50% RH). In addition, a friction trace is shown for a DLN coated Si_3N_4 ball sliding against a DLN coated Ni-Mn moat.

4. Application to LIGA-Fabricated Parts

LIGA-fabricated MEMS parts have unusual morphologies even at the microscopic level, most notably on their sidewalls. So, the challenge is to apply the coating conformally on the sidewalls of LIGA fabricated parts. As discussed earlier, handling of individual LIGA-fabricated Microsystems parts is extremely difficult. Our attempts to prepare the parts by tying them with a thin wire were unsuccessful, thus we have devised a novel strategy specifically tailored to coat the LIGA-fabricated parts. A typical LIGA processing involves the following major steps: (i) creation of a micromold by deep x-ray lithography, typically consisting of PMMA (ii) mold filling by electroplating, (iii) planarizing the filled mold, and (iv) releasing the parts from the wafer. Instead of handling the individual LIGA parts during deposition, we have used the entire wafer after the mold material was dissolved, with parts standing proud of it. The DLN coating was applied by aforementioned PECVD process. The coated wafer was backsputtered to remove the coating material from the planar surfaces of the parts and the wafer. The step is essential to facilitate release chemicals to attack the bond layer, and release the parts from the wafer. The ion etch conditions for DLN in argon gas were RF power 263 W, beam current 170 A, and beam voltage 484 V for a total time of 1 minute and 15 seconds.

Optical micrographs of a 100 nm thick DLN coated wafer with assorted LIGA parts are shown in Fig. 13a. Fig. 13b shows an SEM image of the released parts after backsputtering. A focused ion beam (FIB) cut was taken from the sidewall of the coated part of the gear tooth for SEM analysis (Fig. 14a). Cross-sectional SEM confirmed that the 100 nm thick DLN coating was intact, practically unaffected during backsputtering and subsequent release (Fig. 14b). EDS measurements taken from the cross-section of the coating (Fig. 14c) show carbon, silicon, and oxygen Kα X-rays confirming the constituents of DLN.

We have also used micro-Raman spectroscopy with 1 μm horizontal resolution to verify whether the chemistry of the DLN on planar LIGA Ni tribology test coupons is the same as the sidewalls of LIGA parts [2]. It was surprising to note that though cross-sectional microscopy revealed that the coating was present on the sidewalls, micro-Raman spectroscopy revealed that the initial composition of the coating on the sidewalls was graphitic in nature, and differed from the diamond-like nature of the coating on the planar surfaces (Fig. 15a). The Raman spectrum from sidewalls showed deconvoluted peaks at 1375 cm^{-1} and 1575 cm^{-1}, indicative of graphitic carbon (similar to the transfer film shown in Fig. 6), while the broad peak at 1535 cm^{-1} is indicative of diamond-like

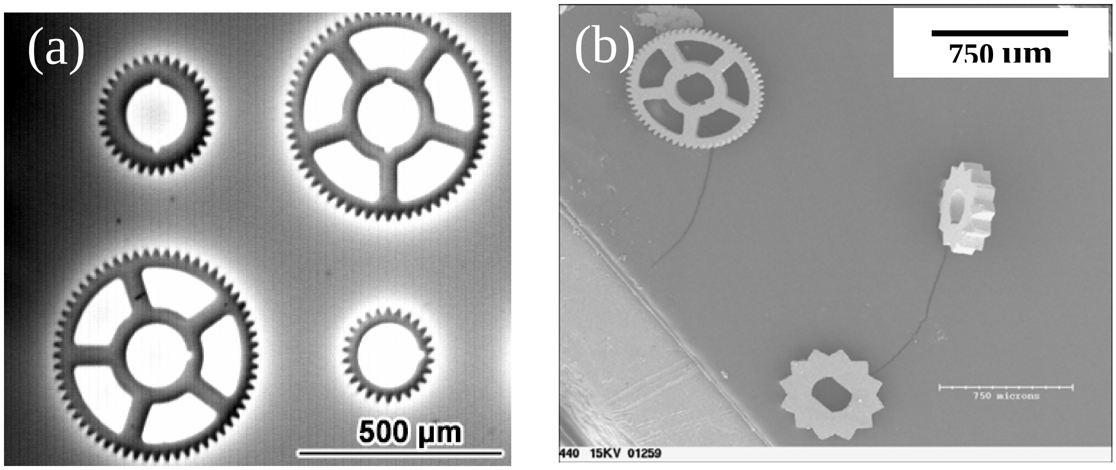


Figure 13. SEM secondary electron images of (a) LIGA fabricated components unreleased from the wafer that were coated with a 100 nm thick DLN coating, and (b) the released components after backsputtering.

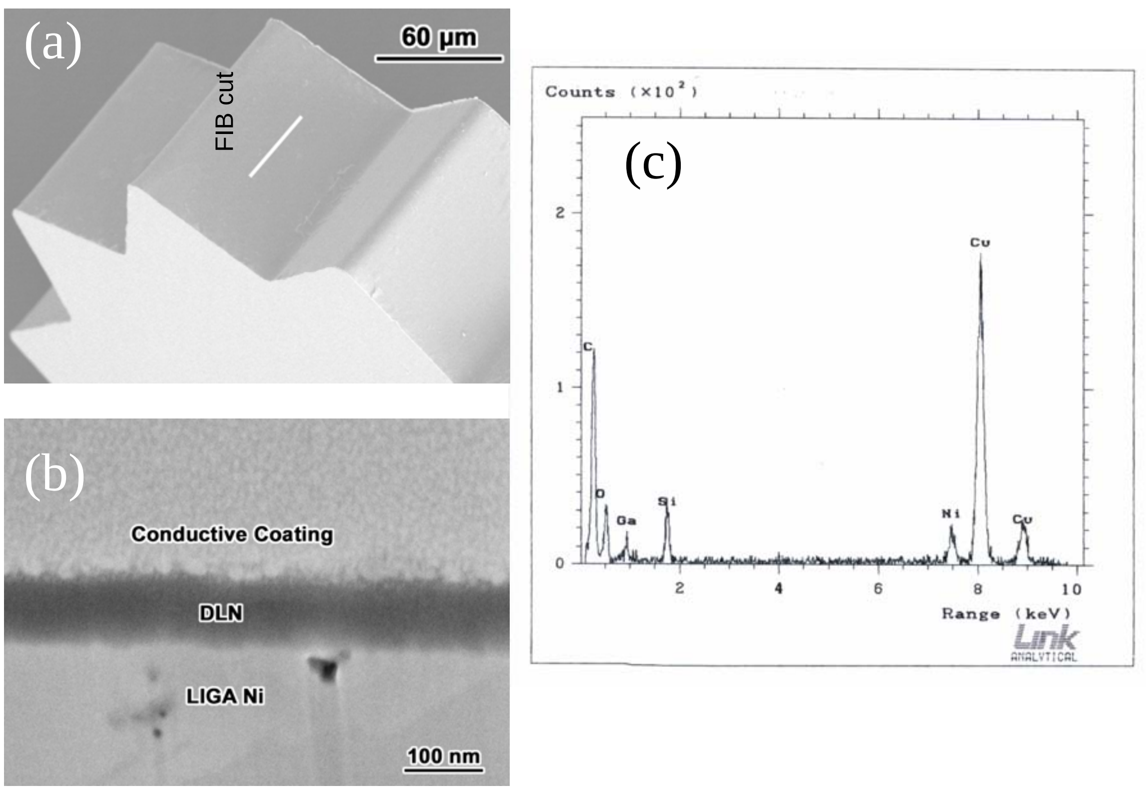
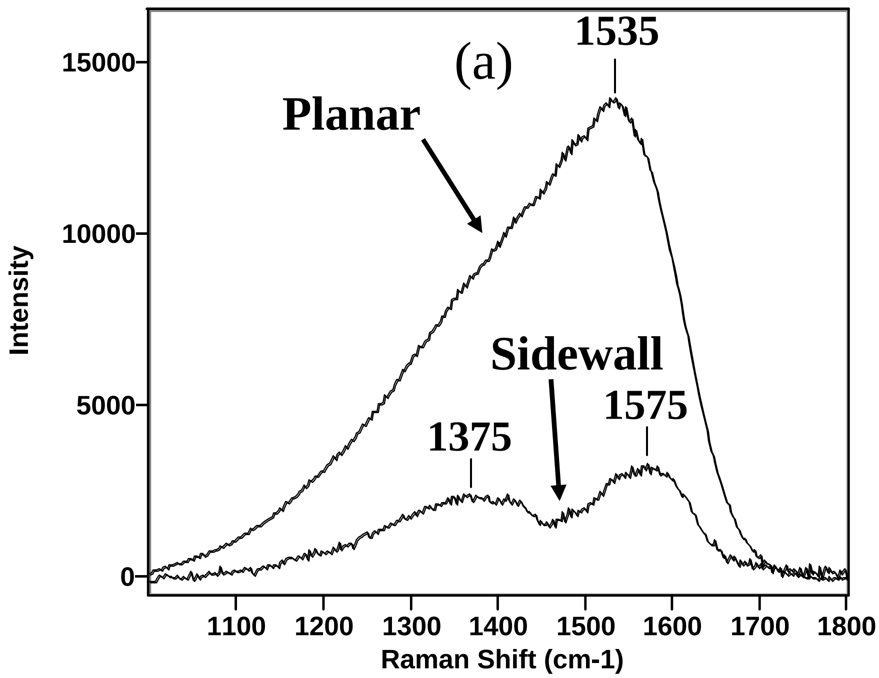


Figure 14. (a) SEM image of a DLN coated LIGA Ni gear, and the location of a FIB cut taken from the sidewall. (b) Cross-sectional SEM image from the FIB cut shows an approximately 100 nm thick DLN coating on the gear sidewall without any interfacial porosity. (c) EDS spectra has the peaks (O, C, and Si) corresponding to the three elements in DLN.



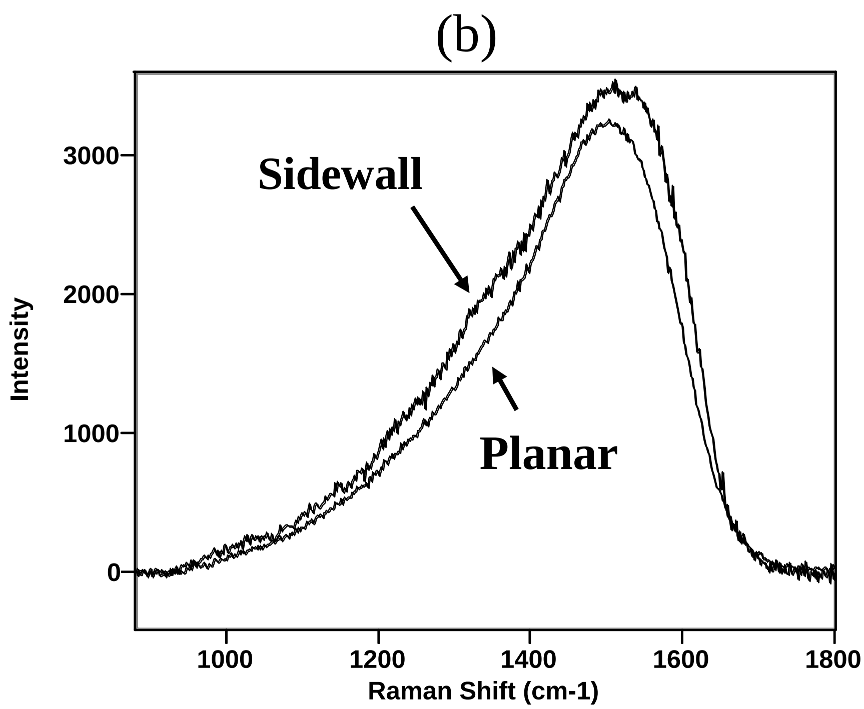


Figure 15. Micro Raman spectra of DLN coating (a) without substrate rotation, and (b) with planetary substrate rotation collected from planar and sidewall surfaces.

carbon. Therefore, the deposition technique was modified to obtain the diamond-like structure on the sidewalls identical to that on the planar surfaces, by introducing planetary substrate rotation. In this scheme, samples are rotated individually on a platen that also rotates at an angle to the source, thereby exposing all surfaces for coating. As a result, Raman spectra from the coatings on LIGA Ni tribology test coupons and on the sidewalls of LIGA Ni parts are identical in nature (Fig. 15b). Thus, we believe that the tribological behavior of the DLN coating on the sidewalls of LIGA parts from the modified process described here is similar to that on planar test coupons shown in Figs. 2 and 12.

In principle, the procedure described here can be applied to deposit any tribological coating. For line-of-sight processes, the substrates must be fixtured in such a way that the deposited material can form on the sidewall surfaces. Substrate rotation alone may not suffice, and planetary motion may be required to expose all sidewall surfaces to the source. Then the coating must be removed from the planar surfaces to facilitate releasing the parts and to preserve edge geometry. Backsputtering conditions and time must be optimized for the type of coating and its thickness. Obviously, the aspect ratio of small holes or other reentrant features on the sides of LIGA parts may preclude coating them uniformly. We addressed this issue for DLN coated LIGA fabricated Ni-Mn moats with 0.012 in. and 0.016 in. holes drilled through its sides (Fig. 16a). Raman spectra of the DLN coating (Fig. 16b) showed both the planar and sidewall surfaces exhibit the exact same chemistry due to the aforementioned planetary rotation during deposition. Transverse cross-sectional cuts were made on the moats through the holes to determine if coating thickness was uniform. An SEM image shown in Fig. 16c of one of the cuts through the 0.012 in. hole shows conformal coverage of the hole with ~190 nm thickness of DLN coating, which is in relatively good agreement with the ~160 nm thickness measured on the planar surface. Thus, the PECVD process efficiently coats small features of parts this size. However, part handling may become problematic if the parts contain millimeter and sub-millimeters dimensions. Instead of handling the individual LIGA MEMS elements, the aforementioned coating of the entire wafer before releasing the parts, i.e. after electroforming, lapping and dissolving the PMMA mold material, is one of the viable options.

5. Summary and Conclusions

We have demonstrated the feasibility of applying diamond-like nanocomposite (DLN) coatings on LIGA fabricated microsystem parts by a commercial plasma enhanced chemical vapor deposition technique. Planetary substrate rotation during film

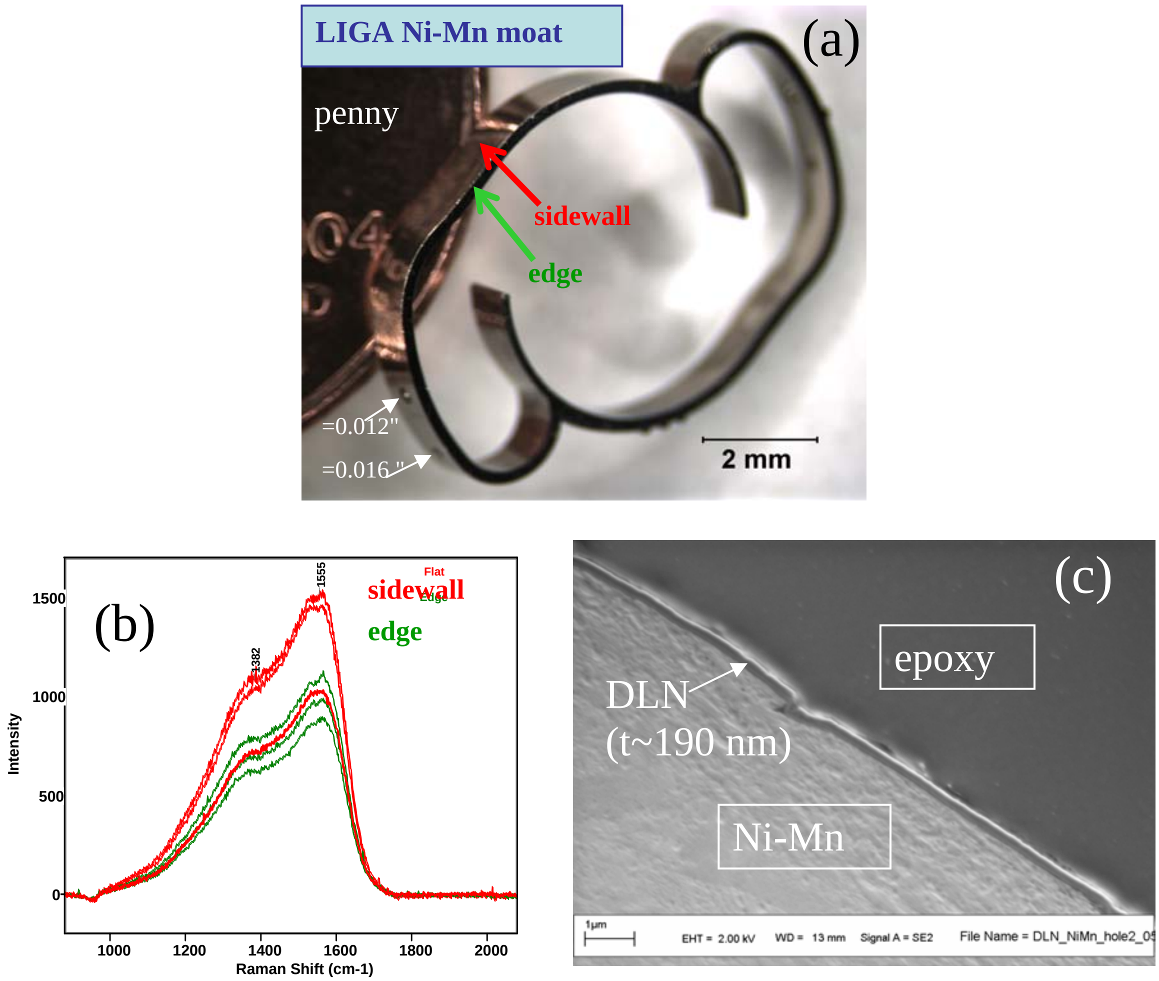


Figure 16. (a) Optical micrograph of a DLN coated LIGA fabricated Ni-Mn moat with 300 µm and 400 µm holes drilled through its sides. (b) Raman spectra of the DLN coating showed both the planar and sidewall surfaces exhibit the exact same chemistry due to planetary rotation during deposition. (c) SEM secondary electron image of a transverse cross-sectional cut made through the 300 µm hole diameter in (a) showing conformal coverage of the hole with ~190 nm thickness of DLN coating.

deposition was found to be essential for getting the diamond-like structure on the sidewalls of LIGA fabricated parts. A novel strategy has been devised to overcome the problems associated with handling miniature LIGA parts during deposition. Characterization studies revealed that the DLN coatings deposited by this modified route were found to have uniform coverage on both planar and sidewall surfaces, as well as inside holes down to 300 μm (0.012") diameter. The presence of a thin titanium bond layer was found to be necessary for the coating to remain adhered during sliding contact. The friction coefficients were very low in both dry nitrogen and ambient air environments, i.e., 0.2 to 0.02, respectively, in comparison to the high values of 0.9 for uncoated Ni-Mn.

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