Pulsed DC Deposition of Near-Frictionless Carbon: Final Report

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Introduction

As part of our ongoing attempts to commercialize Argonne's Near-Frictionless Carbon (NFC) coatings, CemeCon, Inc. arranged for the loan of a Pinnacle Plus pulsed DC power supply with ancillary support equipment and appropriate sputter targets for the deposition of CemeCon's graded Cr-based bond coat. A process engineer from CemeCon AG also came to Argonne to install and operate the new power supply, and work with ANL scientists on process development.

Experimental Procedure

Because the current generation of CemeCon deposition systems uses dual turbopumps and four cathodes, deposition methods for the bond coat could not be applied to Argonne's single-turbopump, two-cathode system without modification. Hans-Gerd Fuss, the CemeCon AG process engineer, began his work at Argonne by altering the deposition method and coating some test pieces with CemeCon's DLC3000. The samples included an unhardened H-13 tool steel disk 2" in diameter, two 3/8" diameter 52100 steel balls, and a pair of pieces of single-crystal silicon wafer.

Following the deposition, tribological tests were done on the coated flat and one of the coated balls using a CSEM room-temperature pin-on-disc tribometer. The first test was done in open air at 40% relative humidity, and the second was done in dry N_2. Load was 2 N, and speed was ca. 60 rpm. The thickness of the coating was measured on one of the coated Si pieces using a CSEM Calotest unit, and the adhesion was measured on the H-13 flat using a Rockwell C indenter.

After the wear test, Raman spectra were collected from the unworn area of the flat, from the wear track, and from various locations on the Calotest crater. Specifically, spectra were taken from different parts of the bond coat exposed on the sides of the crater.

Deposition conditions for the attempts at NFC are summarized in Table 1, and the justification will be covered in the Results/Discussion section. In each of the three attempts, a hardened 52100 steel flat, two 52100 9mm diameter steel balls, and two pieces of single-crystal silicon wafer were coated. The steel flat and one of the Si pieces were mounted vertically on an aluminum triangular prism fixture, the other Si piece was set horizontally near the top of the chamber, and the two balls were mounted on nuts around halfway up the chamber. In the first two attempts, three cylindrical steel test pieces were also coated, to determine the top-to-bottom thickness uniformity of the deposition. They were placed in appropriate tower fixtures near the bottom, at the middle, and near the top of the chamber.

After the NFC deposition, Raman spectra were collected on the steel flats and the silicon pieces (where applicable). Where possible, tribological tests were performed on the steel flats and balls, in dry nitrogen and in open air, under loads of 5 N or 10 N, for up to 30 000 seconds. Adhesion tests were performed on all three steel flats using a Rockwell C indenter, and Rockwell C hardness values were also recorded.

Following the tribological tests, Raman spectra were collected on the balls coated in the second and third attempts, as the coating quality there did not seem to be as good as that on the flats.

Results/Discussion

Thickness measurements on the DLC3000 coating (Figure 1) showed that the diamondlike carbon top layer on the flat was ca. 1.5 µm thick, and the graded CrN-CrCN-CrC bond coat was ca. 2.5 µm thick. The adhesion of the DLC3000 was excellent (Figure 2); its friction and wear performance was less so (Figure 3). In open air transient (<30 seconds) low friction was observed, but then the friction coefficient rapidly climbed, reaching ca. 0.3 in around 30 minutes. The friction coefficient then fell slowly. In dry N_2, the friction coefficient was again initially low—ca. 0.02—but rapidly climbed to ca. 0.11 after 30 minutes, where it stabilized for the rest of the test.

The results of the Raman spectroscopy are given in Figures 4a-4d. It is clear that there is still DLC coating in the wear track, and thus that the reason for the increase in friction is not the exposure of the underlying bond coat: None of the bond coat layers have Raman peaks corresponding to the DLC G and D peaks, but these appear strongly in the wear track spectrum.

After establishing that DLC3000 could be deposited using the ANL system with the pulsed DC power supply, a first attempt at a method for NFC deposition was devised. All of the previous NFC coatings deposited using the CC800 were either from pure methane or methane/1-2% hydrogen source gas plasmas. For the first attempt, though, it was decided that the source gas composition should be 75% methane/25% hydrogen (i.e., equivalent to NFC 8), with gas flows of 120 sccm methane/40 sccm hydrogen. It was known from Osman Eryilmaz' work with the Perkin-Elmer that NFC could be deposited with self-bias voltages as low as 250V, but with rather lower deposition rates than at the more typical 500V. To reduce the possibility of overheating, pulsed bias voltage was set to 350V. Pulse frequency was 250 kHz (but see below), reverse time was 1.6 µsec, and deposition time was 2 hours. Instead of the graded DLC3000 bond coat, a thin layer of sputtered Cr was used to promote adhesion. Chamber pressure during the DLC deposition was ca. 2 Pa (ca. 15 mTorr). In general, the plasma seemed dimmer than was observed in the Perkin-Elmer coating system (but see below). Pulsed DC current reached 2.1 A, for a total power level of 730W.

The results were mixed. Film adhesion on the steel flat, the balls, the vertical Si piece, and one of the cylinders was extremely poor, as large areas of the film flaked off readily in the absence of mechanical loading. However, Raman spectra of the still-adherent areas on the steel flat and on the horizontal Si piece showed that the coating was highly amorphous, indicating little or no excess heating (Figure 5). This was confirmed by a Rockwell C hardness test on the steel flat; the hardness was still HRC 62, and 52100 steel is prone to softening at relatively low (ca. 125-150°C) temperatures. The photoluminescent background was rather lower than that seen with other NFC coatings, suggesting that the film hydrogen content was lower even than that of NFC 7 (shown in Figure 5 for comparison).

The adhesion problems may have been due to the bond coat composition, or they many have arisen from changes in the instrument conditions during the first several minutes of DLC deposition. In the run parameters, the Cr cathode had 1000W on it at the onset of DLC deposition. This brought about very high chamber pressure before it was turned off (>3 Pa or >23 mTorr), and the plasma was quite bright. We believed these

were caused by a sharp increase in plasma ionization in the chamber, resulting in a more energetic plasma (thus, the brightness) and more methane fragmentation (thus, the increase in pressure as the plasma hydrogen content increased). The pulse frequency was also initially 350 kHz, but was decreased to 250 kHz after a few minutes. After a couple of minutes of deposition, 500W was applied to the graphite target briefly. Again, the plasma rapidly grew brighter and the pressure began to increase. All of these variations may have resulted in poor coating quality in the critical region directly adjacent to the bond coat, bringing about the observed problems with adhesion.

For these reasons, the parameters for the next run were changed so as to use the DLC3000 bond coat, no changes were made during the DLC deposition, and the source gas composition was 50% methane/50% hydrogen (i.e., equivalent to NFC 2) , with gas flows 80 sccm each methane and hydrogen. Pulse frequency was 250 kHz, reverse time was 1.6 µsec, pulse bias was 300V, and deposition time was 3 hours. The same types of samples were coated as in the first attempt at NFC; i.e., 52100 steel flat, 440C steel balls, Si wafer pieces, and cylindrical test pieces. The bias was reduced because the increased hydrogen content of the plasma had the potential to cause higher ion flux onto the samples during deposition, increasing sample heating. Chamber pressure during coating ranged from ca. 2 Pa (ca. 15 mTorr) at the beginning of the run to ca. 2.3 Pa (ca. 17.5 mTorr) at the end. The plasma was fairly dim, and by the end of the run the DC current was ca. 2.0 A, for a DC power level of ca. 600W.

On removal from the chamber, the coatings looked good. They were definitely thin on the cylinders and Si pieces, but appeared glossy black on the steel flat and balls. No spontaneous delamination took place as the parts cooled. In fact, adhesion was quite good (Figure 6), and Rockwell hardness of the steel flat was still HRC 62. Raman spectra on the coatings on the vertical steel flat and Si piece looked nearly identical to those from the previous run (Figure 7). The tribological test results, however, were excellent (Figure 8). Testing was done on the CSEM room-temperature pin-on-disc tribometer, under a 5 N load, at 300 rpm, in dry N_2. The friction coefficient after 1 hour was ca. 0.006. The only reason the wear track on the flat can readily be seen (Figure 9) is from the presence of a scratch caused by a flake of coating from the ball side (Figure 10); otherwise, the wear track is indistinguishable from its surroundings in optical profilometry (Figure 11).

Because of the excellent performance of this coating, we elected to further increase the amount of hydrogen in the source gas, to 75% hydrogen/25% methane (i.e., equivalent to NFC 6). Initial flows were 90 sccm hydrogen/30 sccm methane, as hydrogen flow was limited to 100 sccm. Initial pulsed bias was set to 300V, but we decided that we would change it and total gas flow as needed to achieve a chamber pressure of ca. 2 Pa (ca. 15 mTorr). Deposition time was increased to 6 hours, but pulse frequency and reverse time were left unchanged. No cylindrical test pieces were coated in this run, but all other samples were the same. After the run started, we increased the gas flows to 99 sccm hydrogen/33 sccm methane, and increased the pulsed bias to 328V. Chamber pressure peaked at ca. 2 Pa, as intended. Current at the end of the run was not known, but was ca. 1.3 A when the pressure was ca. 1.7 Pa. Current is observed to increase monotonically with chamber pressure.

On removal, the coating looked as good as the previous run. No delamination had taken place while the samples cooled in the chamber. Adhesion was better than the previous run (Figure 12), and the 52100 steel flat did not soften measurably. Raman spectra on the coatings were virtually identical to the last two sets (Figure 13). The

tribological test results were better than the previous run's (Figure 14); friction coefficient under the same conditions reached ca. 0.003, and after ca. 10 hours no wear track was visible on the flat (Figure 15). There was a small facet on the ball (Figure 16), but the coating was still intact. A second test was done under a 10 N load for 30 000 seconds. At the end of that time the ball coating had worn through in one spot (Figure 17), but the friction coefficient was still low (Figure 18) and the wear track on the flat was still very difficult to distinguish (Figure 19). A 5 N 300 rpm open-air test did not go as well (Figure 20), as the coating apparently wore through quickly on the ball side (Figure 21). However, despite the fact that the friction coefficient was as high as 0.11 after the ball coating wore through, the wear rate on the flat side was still extremely low—wear track depth was only a few nm (Figure 22).

Because of the more rapid wear rate on the coated balls, it was believed that they may have overheated during coating, partially graphitizing the coating. The Raman spectra do not seem to bear this out, however (Figure 23); the coatings on both balls appear to be amorphous, and show no signs of crystallization. The Raman spectra on the balls and flats coated at the same time are also nearly identical, indicating that any structural differences between the coatings will be subtle (Figure 24). While performing the Raman analysis, however, it was observed that the ball coatings were somewhat patchy and nonuniform, with small areas where the NFC coating seems to have flaked off. Although it is difficult to pick out details on the ball wear scar micrographs, some small areas of higher reflectivity can be seen in Figure 10. It is possible that the bond coat on the balls was not as effective as the bond coat on the flats, although this does not explain the rapid wear rate in open air. More work needs to be done to determine what is happening.

Conclusions

By any measure, these results are extremely encouraging. It has now been established that NFC coatings can be deposited in the CemeCon CC800/9sx unit using pulsed DC to generate the plasma, and further that the DLC3000 bond coat technology can be used with PACVD coatings. In terms of process variables, it should be possible to increase the deposition rate by increasing either or both the deposition pressure and/or the pulsed bias voltage without adversely affecting the coating quality. Other structural characterization may be performed on the coatings, including fluctuation microscopy, ultraviolet Raman spectroscopy, and near-edge x-ray absorption fine structure spectroscopy.

Table 1: NFC Deposition Conditions

Gas Flows (sccm; CH_4/H_2)	***Deposition Time (hrs)***	***Pulse Frequency (kHz)***	***Pulse Bias (V)***	***Chamber Pressure (Pa/mTorr)***
120/40	2	350	350	1.3 – 1.96/ 10 – 15
80/80	3	250	300	2.03 – 2.34/ 15 – 17.5

Gas Flows (sccm; CH_4/H_2)	***Deposition Time (hrs)***	***Pulse Frequency (kHz)***	***Pulse Bias (V)***	***Chamber Pressure (Pa/mTorr)***
33/99	6	250	328	1.1 – 2.03/ 8.4 – 15

Figures for Pulsed DC NFC Deposition Report

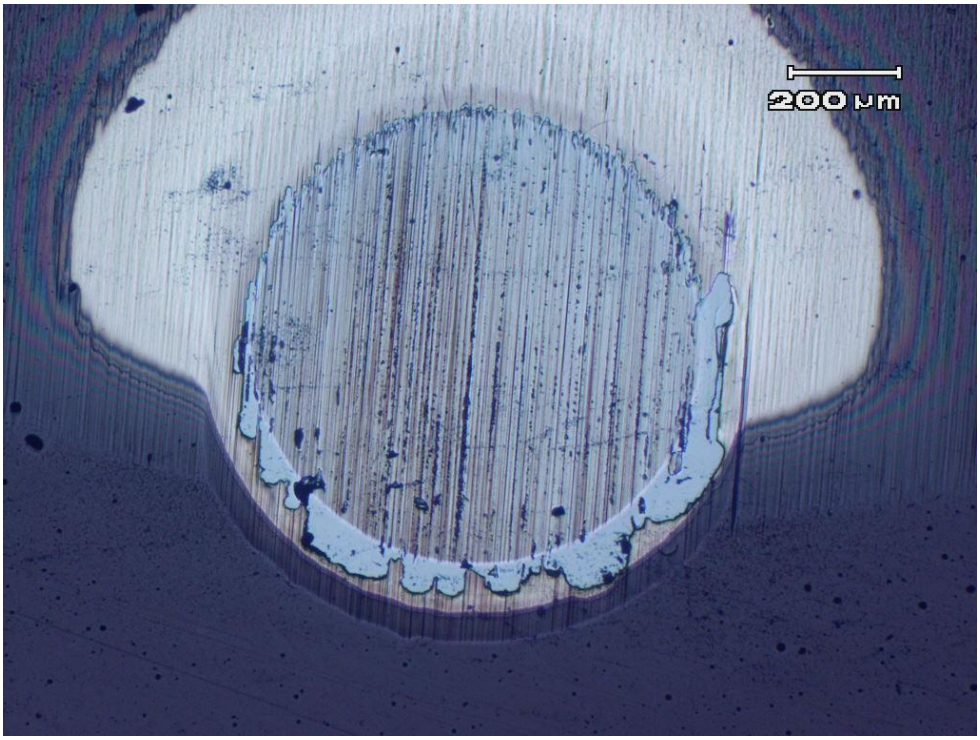


Figure 1: Calotest crater on Si wafer piece coated with DLC3000

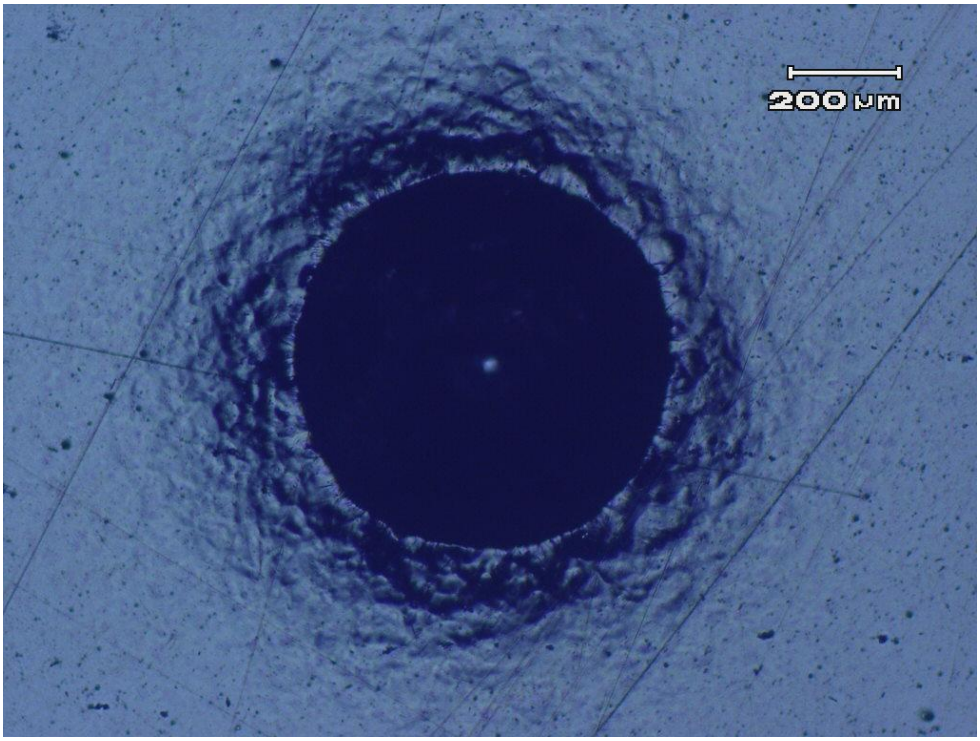


Figure 2: Optical micrograph of Rockwell C indent on the steel flat coated with DLC3000

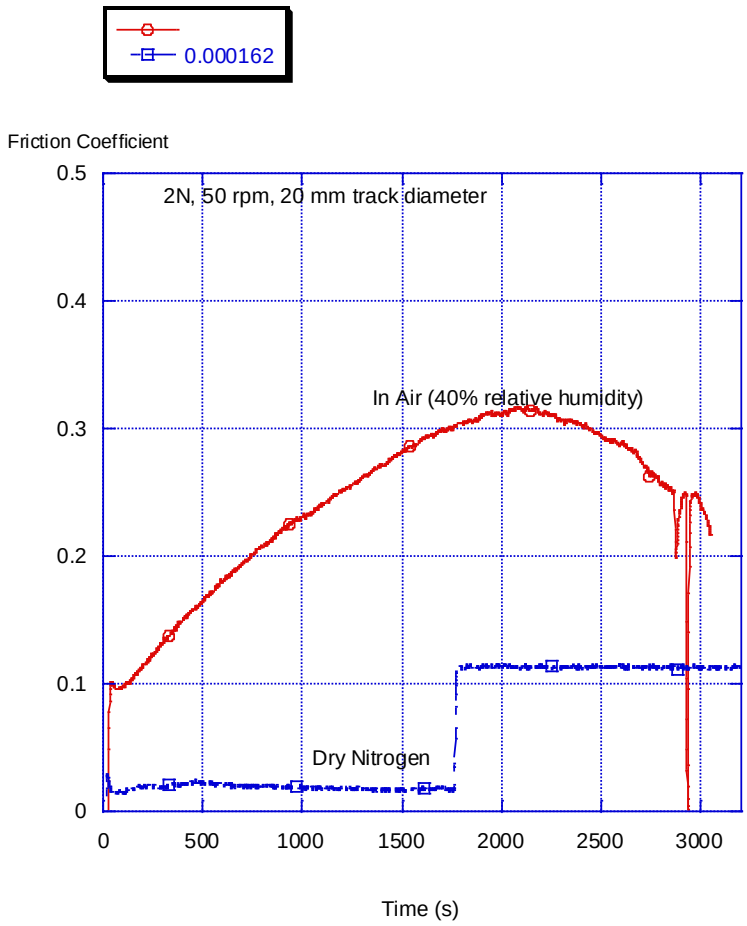
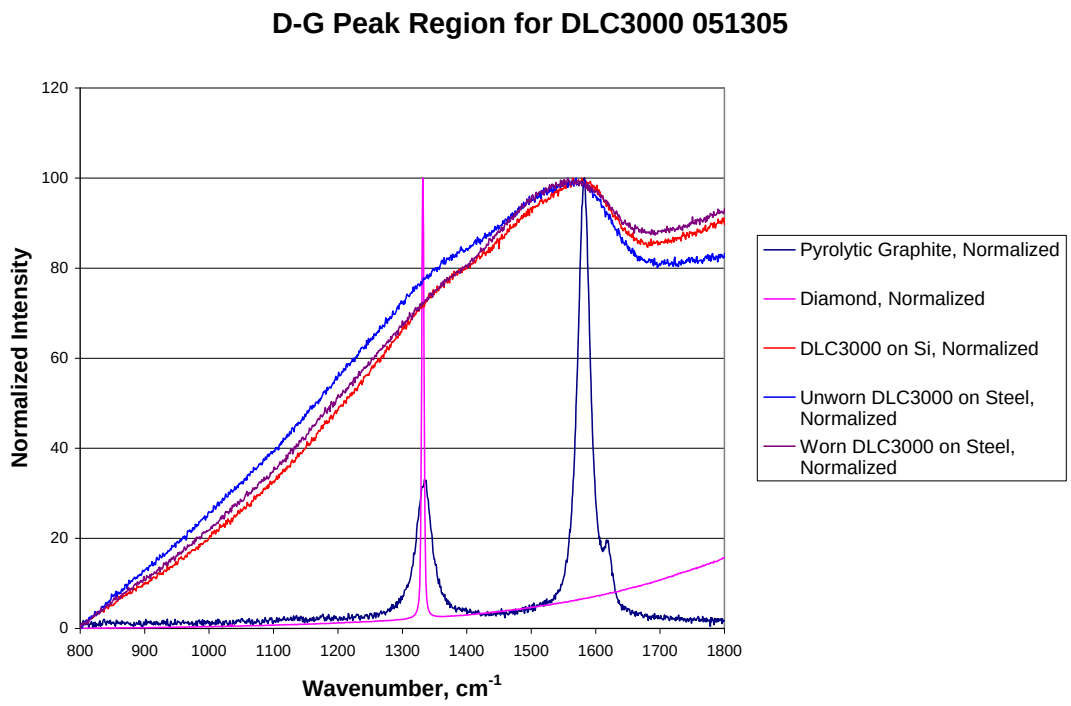
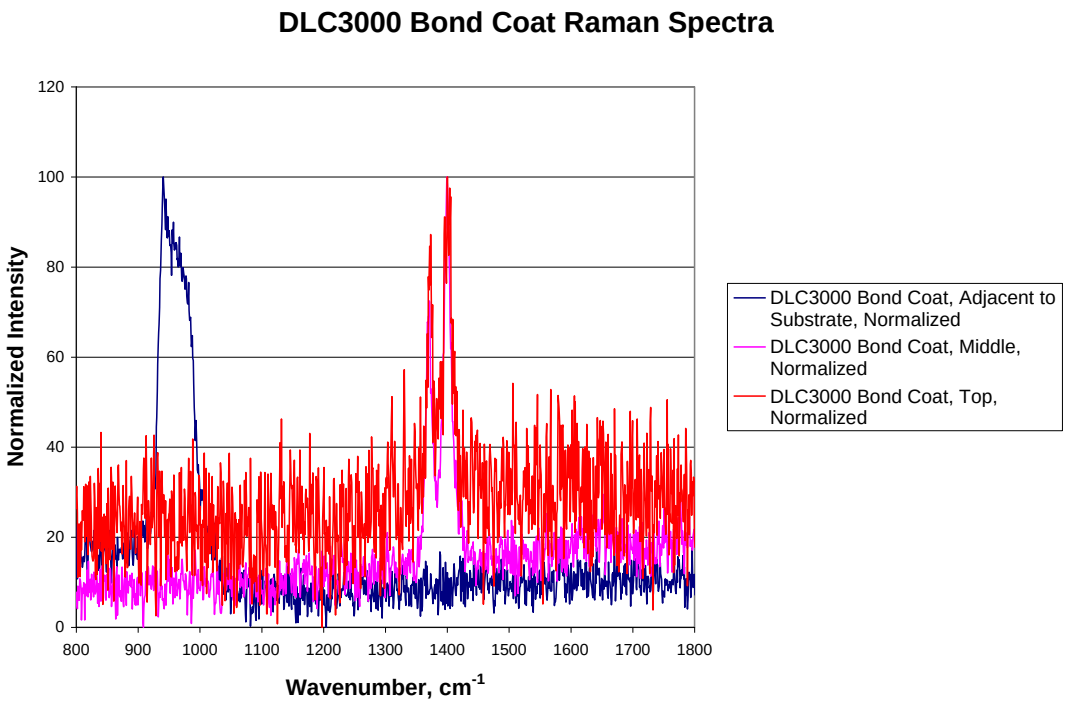


Figure 3: Plot of friction coefficient vs. time for dry N_2 and open air tests of DLC3000, under 2 N load



(a)



(b)

Figure 4: Normalized Raman spectra of the DLC3000 coating; (a) is from the DLC topcoat, both unworn and worn areas, and (b) is from three different areas of the bond coat

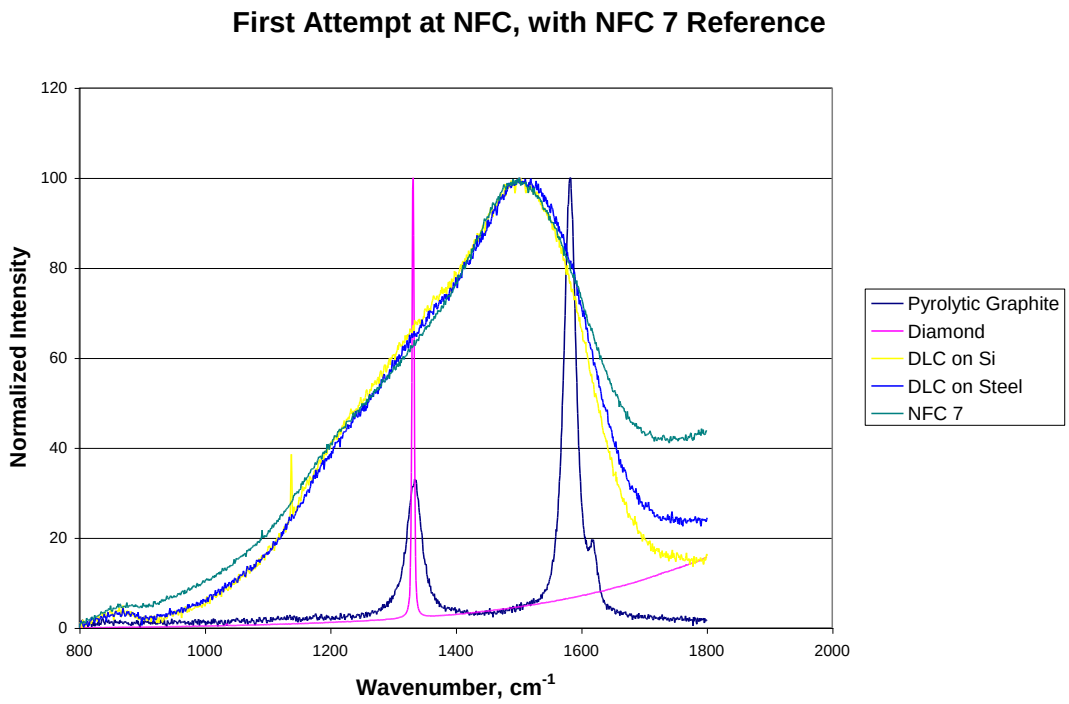
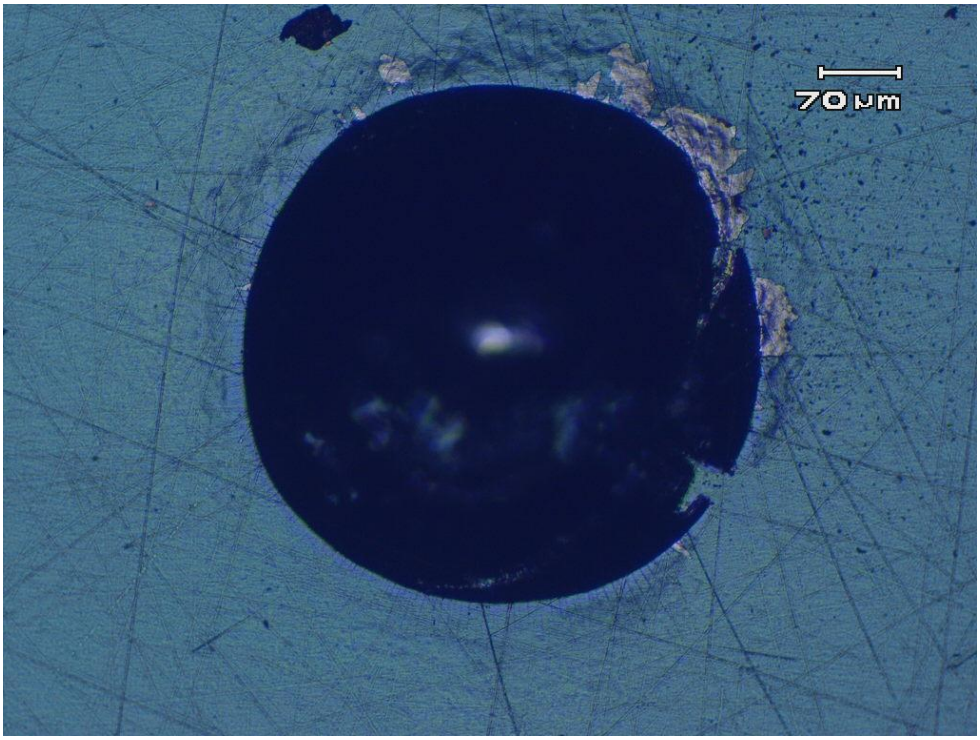
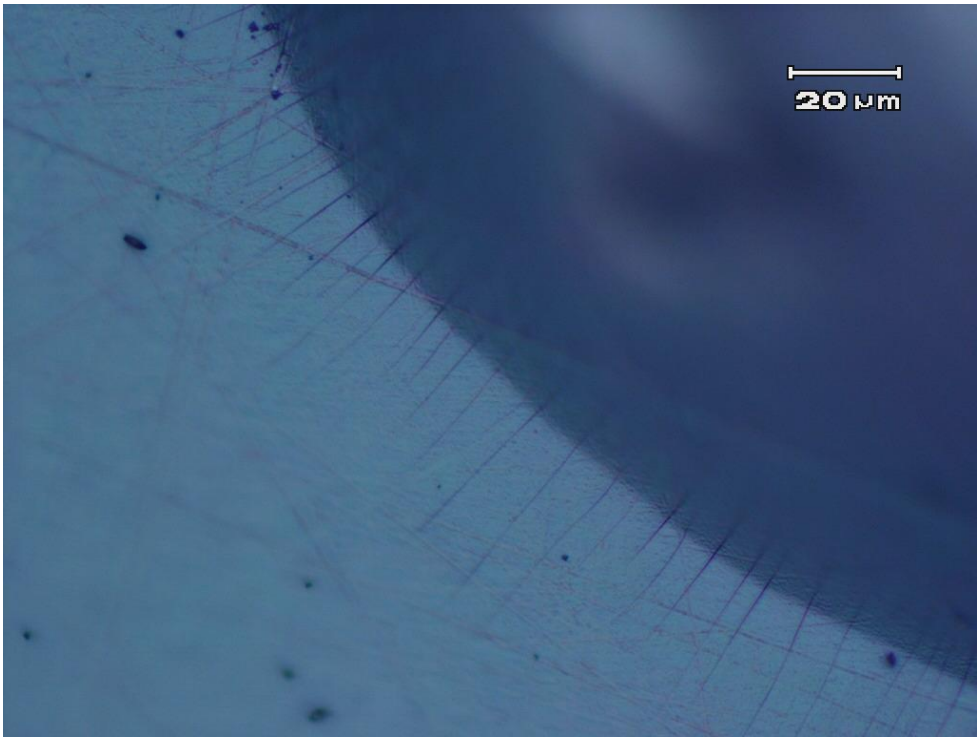


Figure 5: Raman spectra on the vertically-mounted steel and horizontally-mounted silicon samples, coated with the first attempt at NFC, normalized, together with spectra for diamond, pyrolytic graphite and NFC 7



(a)



(b)

Figure 6: Low-magnification (a) and high-magnification (b) optical micrographs of Rockwell C indents on the steel flat coated with the second attempt at NFC

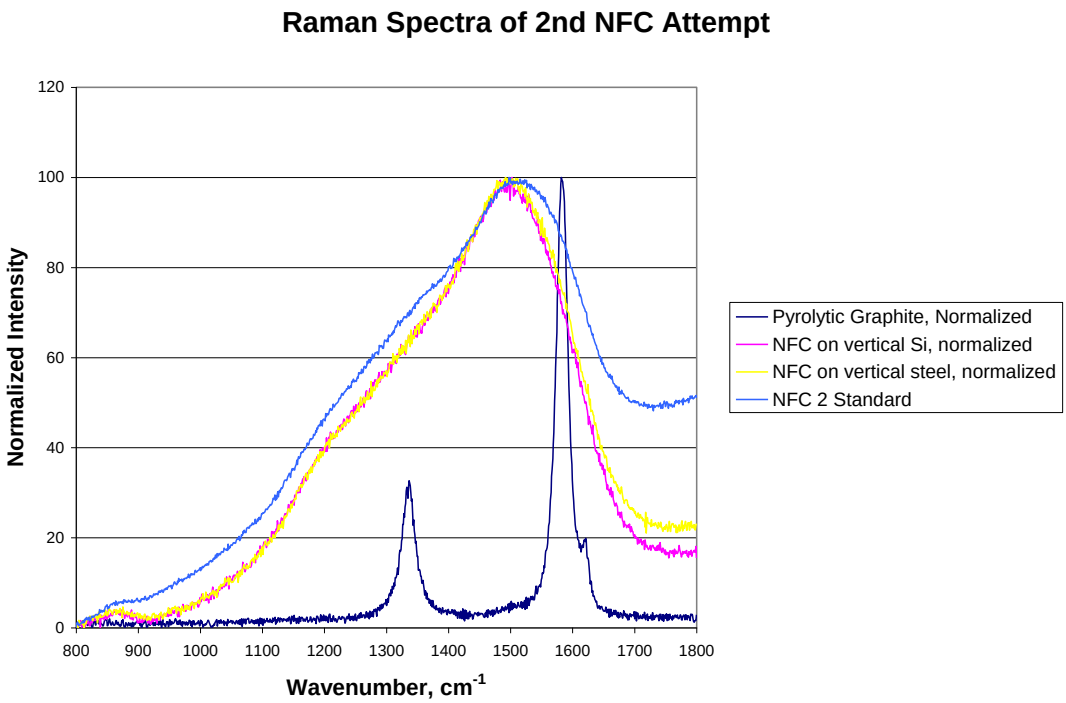


Figure 7: Raman spectra on the vertically-mounted steel and silicon samples coated with the second attempt at NFC, normalized, together with spectra for pyrolytic graphite and NFC 2

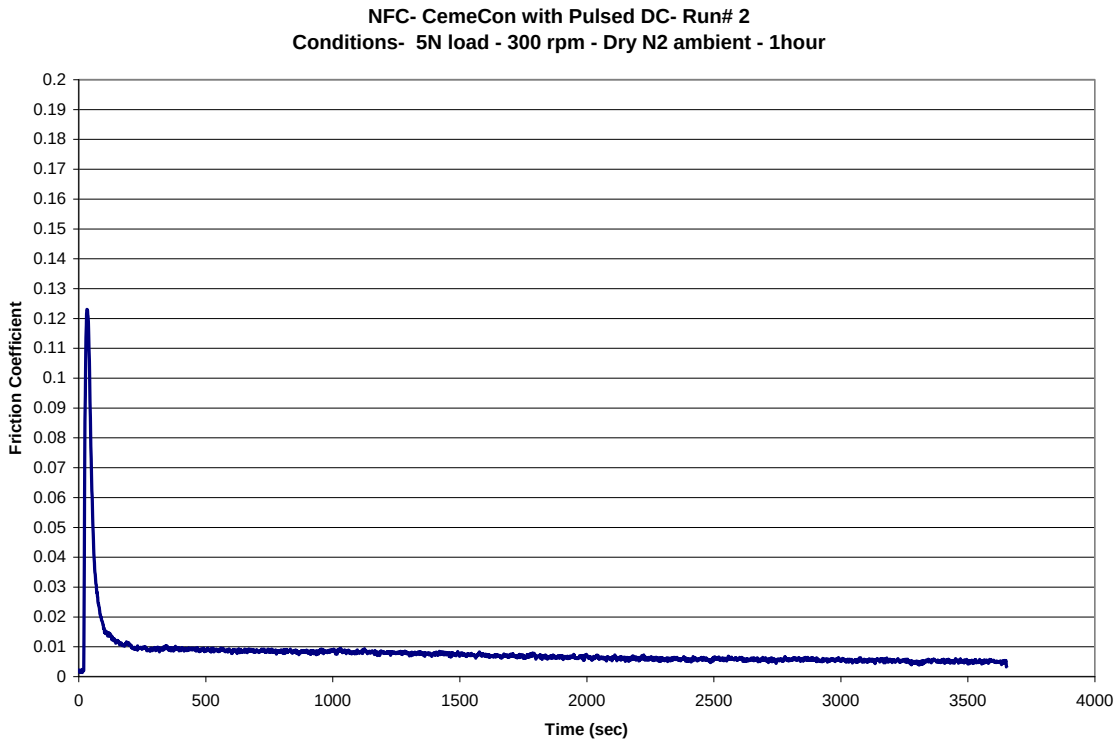


Figure 8: Plot of friction coefficient vs. time for dry N_2 test of the second attempt at NFC, under 5 N load

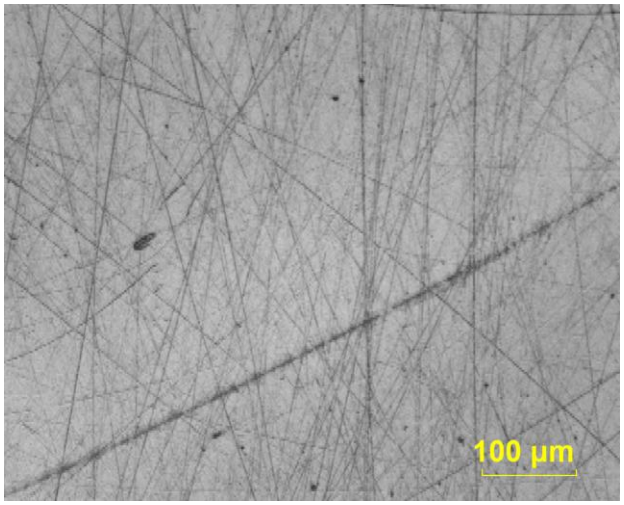


Figure 9: Wear track on the flat coated with the second NFC attempt, tested in dry N_2 under 5 N load

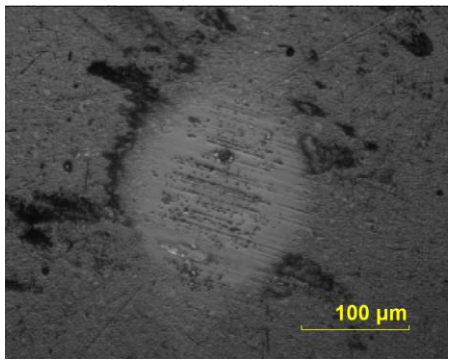


Figure 10: Wear scar on the ball coated with the second NFC attempt, tested in dry N_2 under 5 N load

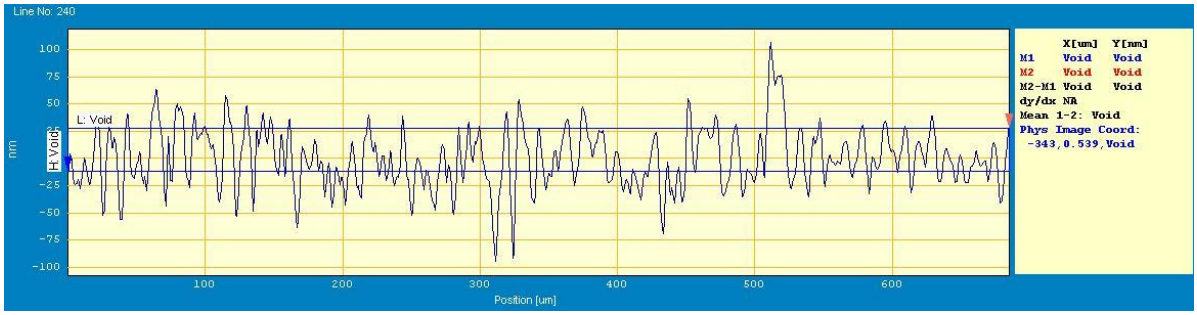
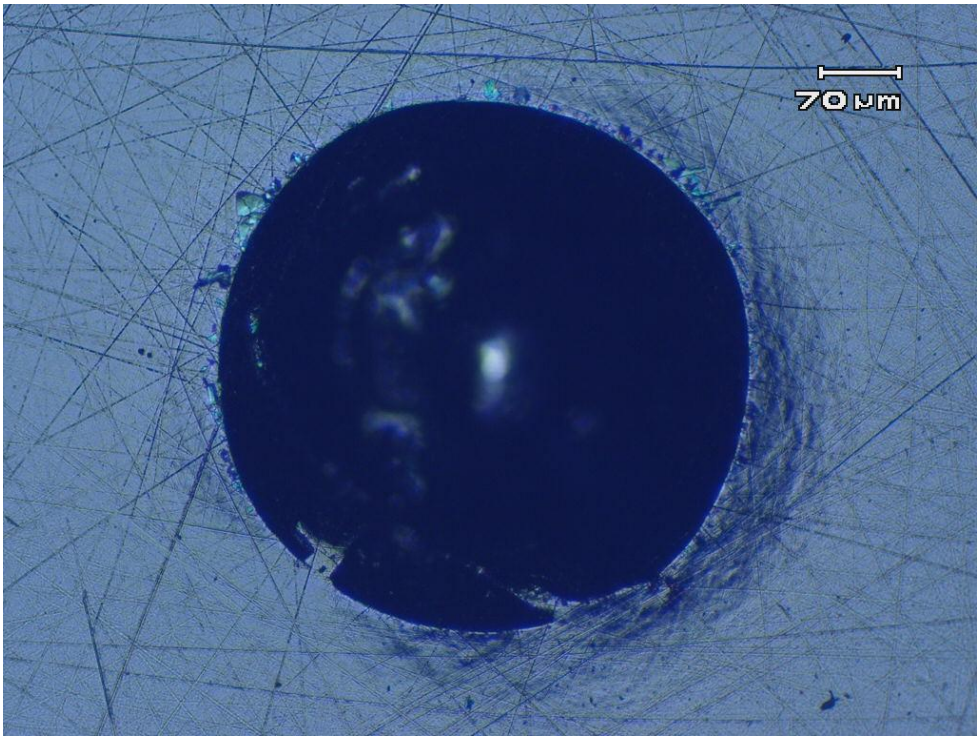
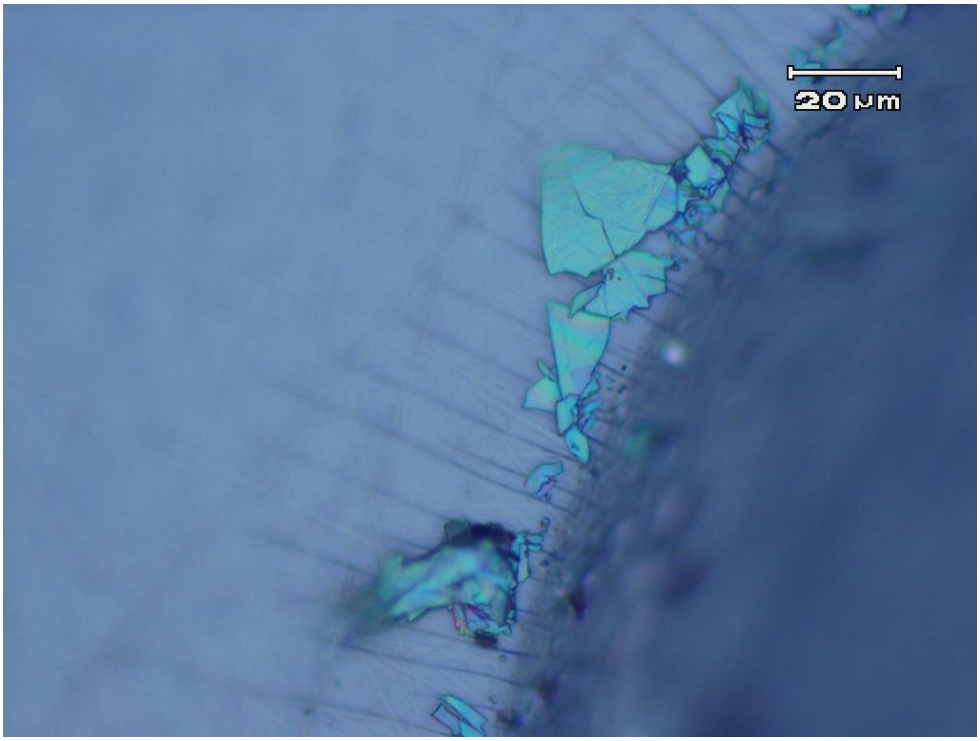


Figure 11: Optical profile of the wear track on the flat coated with the second attempt at NFC after friction test in dry N_2



(a)



(b)

Figure 12: Low-magnification (a) and high-magnification (b) optical micrographs of Rockwell C indents on the steel flat coated with the third attempt at NFC

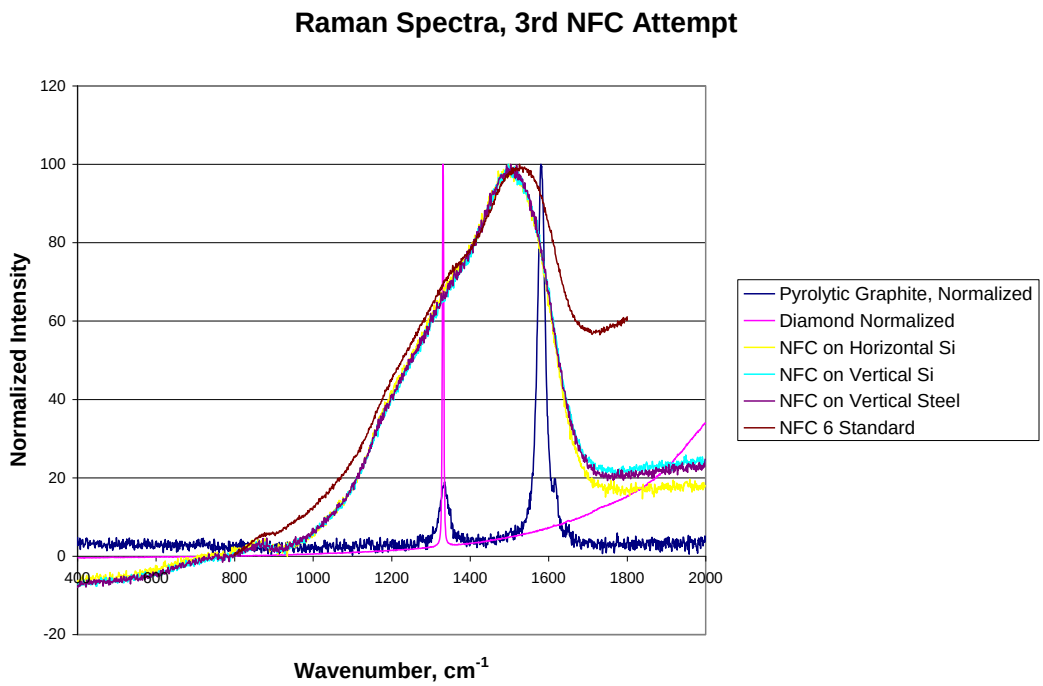


Figure 13: Raman spectra on the vertically-mounted steel and silicon samples, and the horizontally-mounted silicon sample, coated with the third attempt at NFC, normalized, together with spectra for diamond, pyrolytic graphite and NFC 6

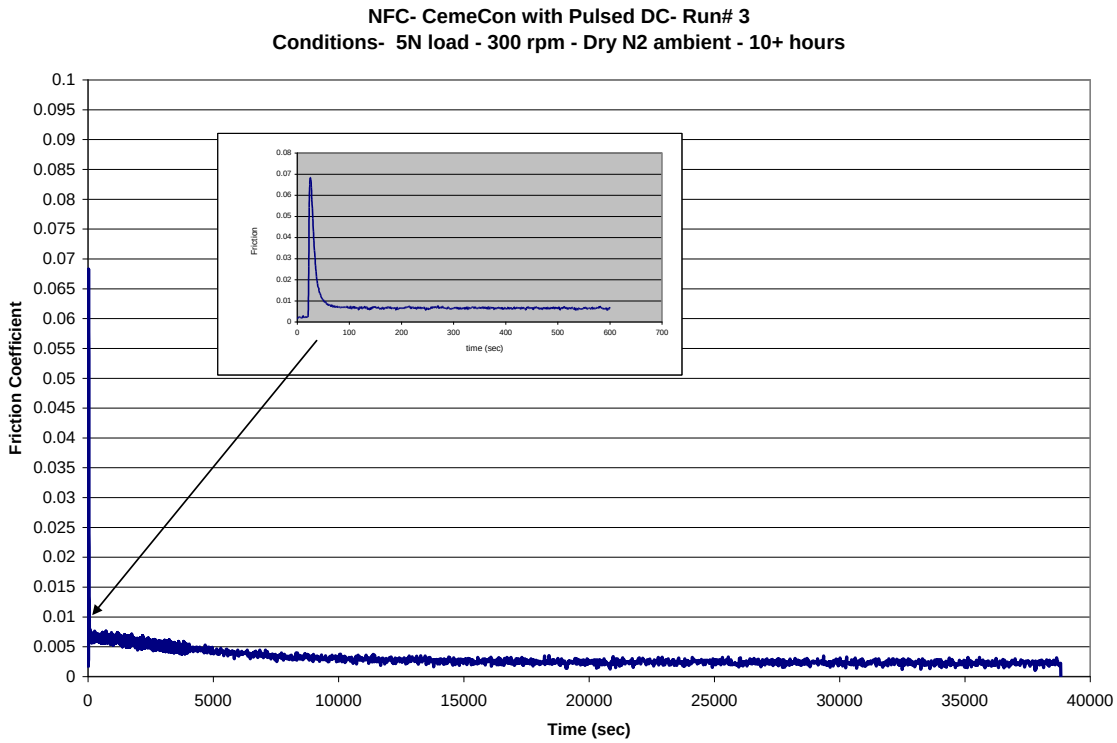


Figure 14: Plot of friction coefficient vs. time for dry N_2 test of the third attempt at NFC, under 5 N load

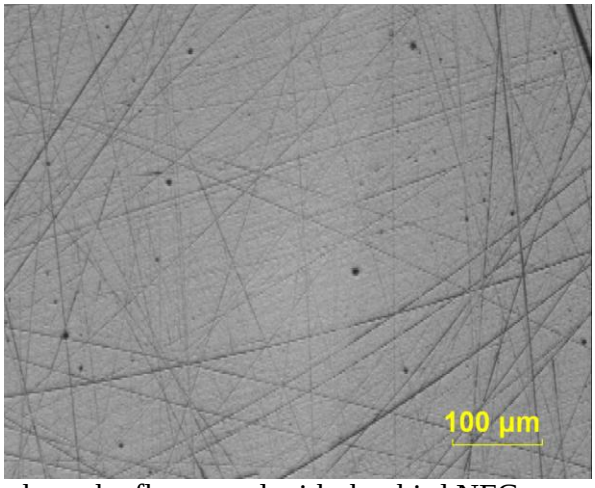


Figure 15: Wear track on the flat coated with the third NFC attempt, tested in dry N_2 under 5 N load

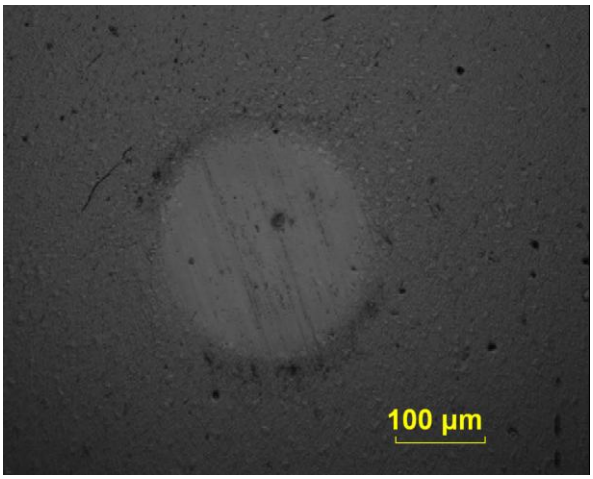


Figure 16: Wear scar on the ball coated with the third NFC attempt, tested in dry N_2 under 5 N load

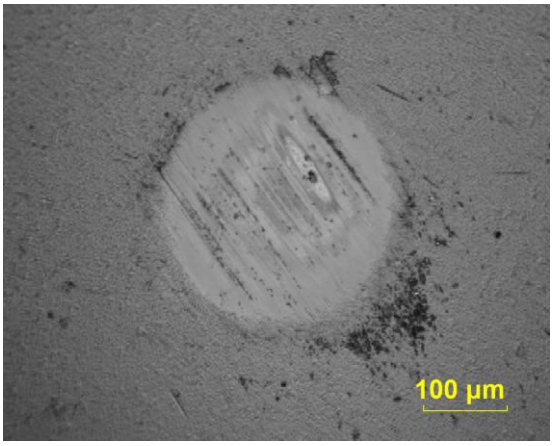


Figure 17: Wear scar on the ball coated with the third NFC attempt, tested in dry N_2 under 10 N load

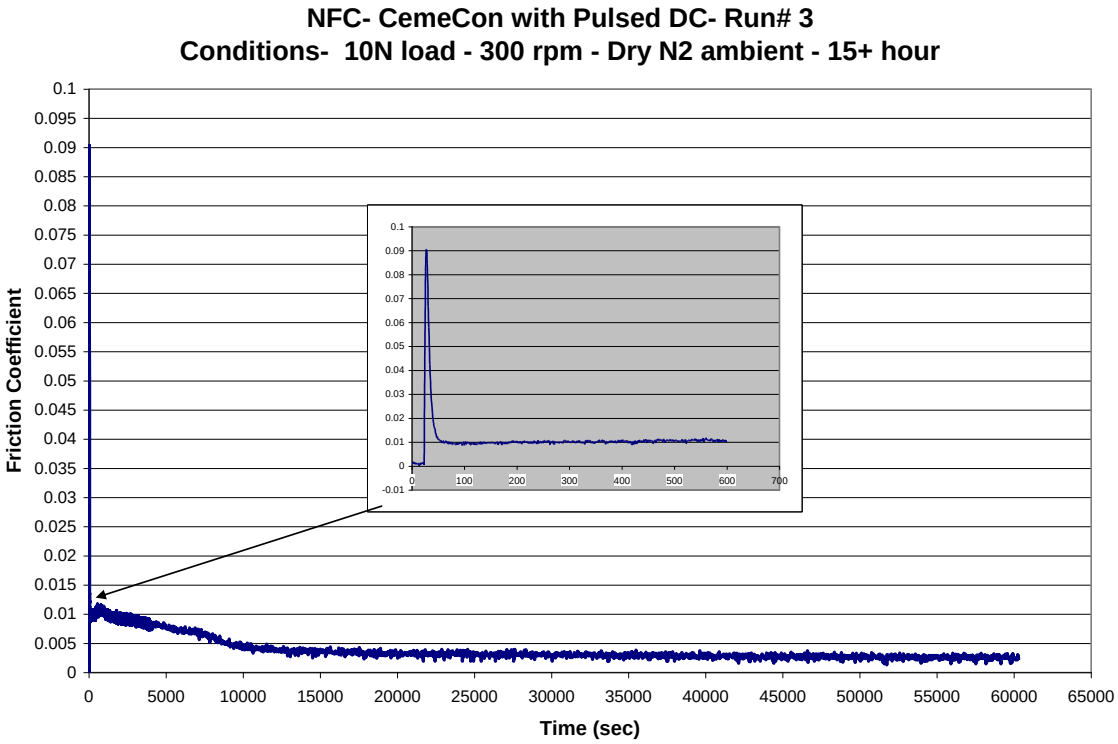


Figure 18: Plot of friction coefficient vs. time for dry N_2 test of the third attempt at NFC, under 10 N load

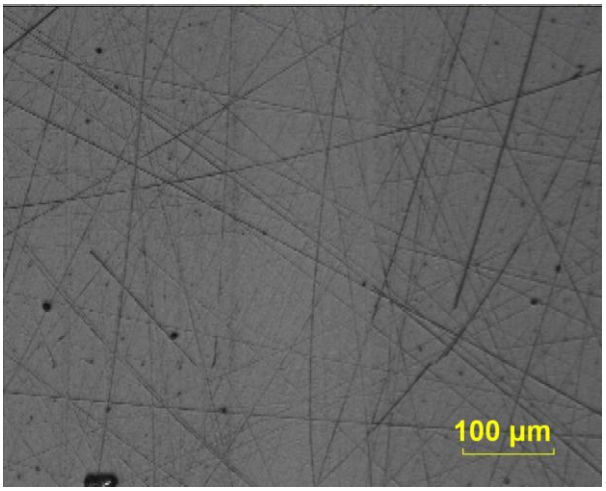


Figure 19: Wear track on the flat coated with the third NFC attempt after the 10 N load friction test

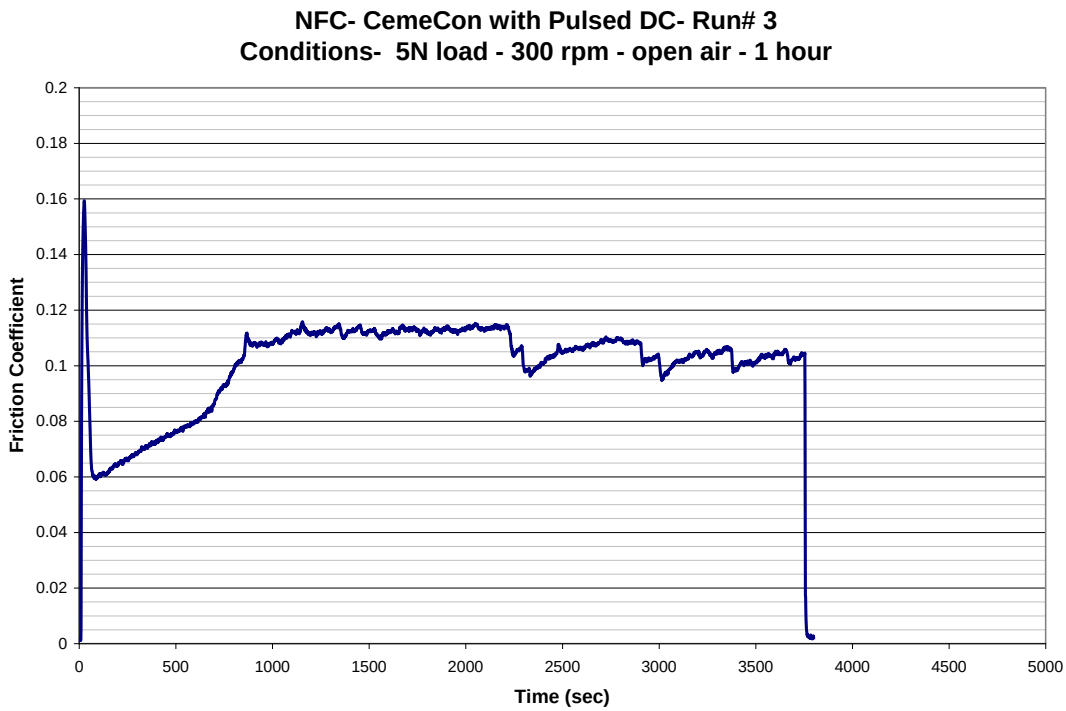


Figure 20: Plot of friction coefficient vs. time for open-air test of the third attempt at NFC

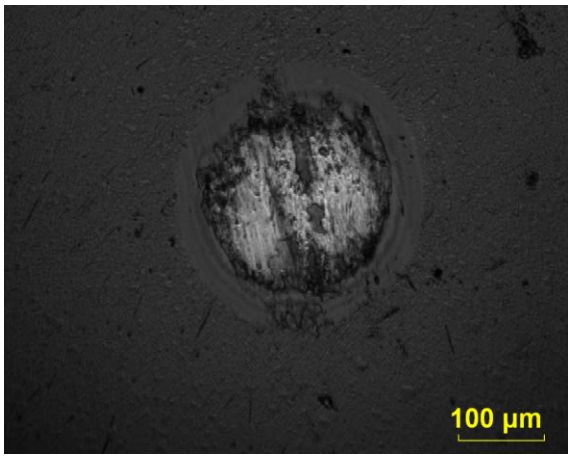


Figure 21: Wear scar on the ball coated with the third NFC attempt, tested in open air

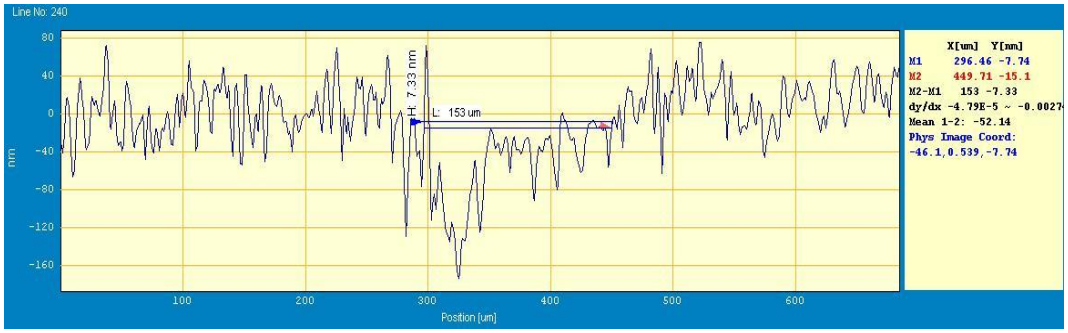


Figure 22: Optical profile of wear track on the flat coated with the third NFC attempt, tested in open air

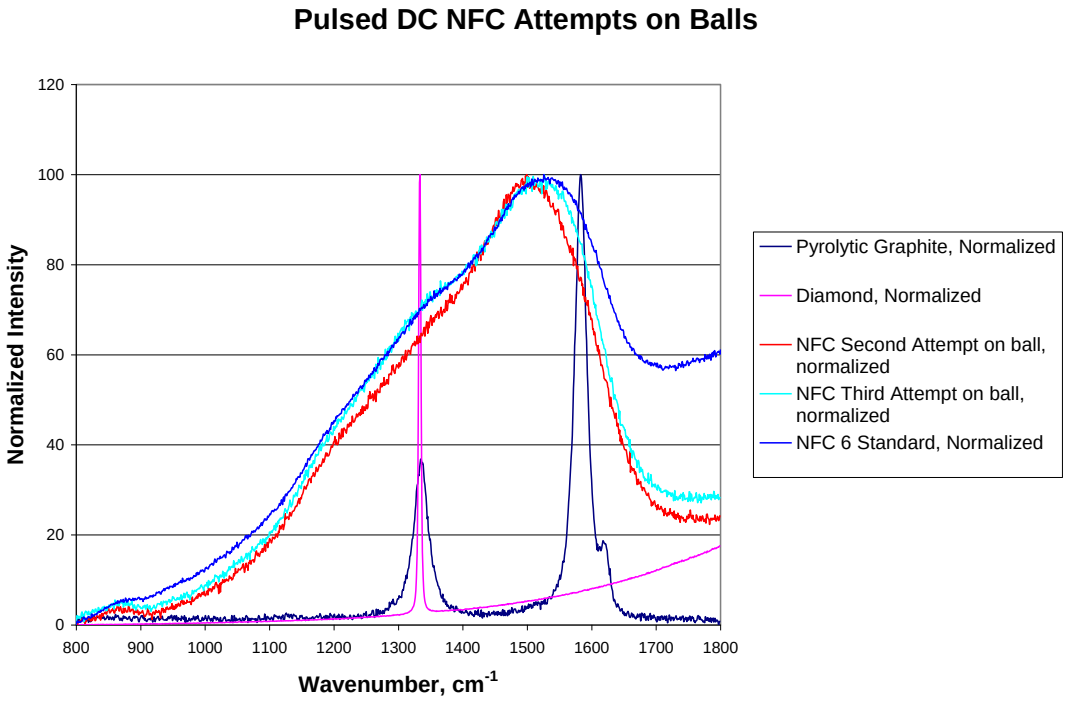
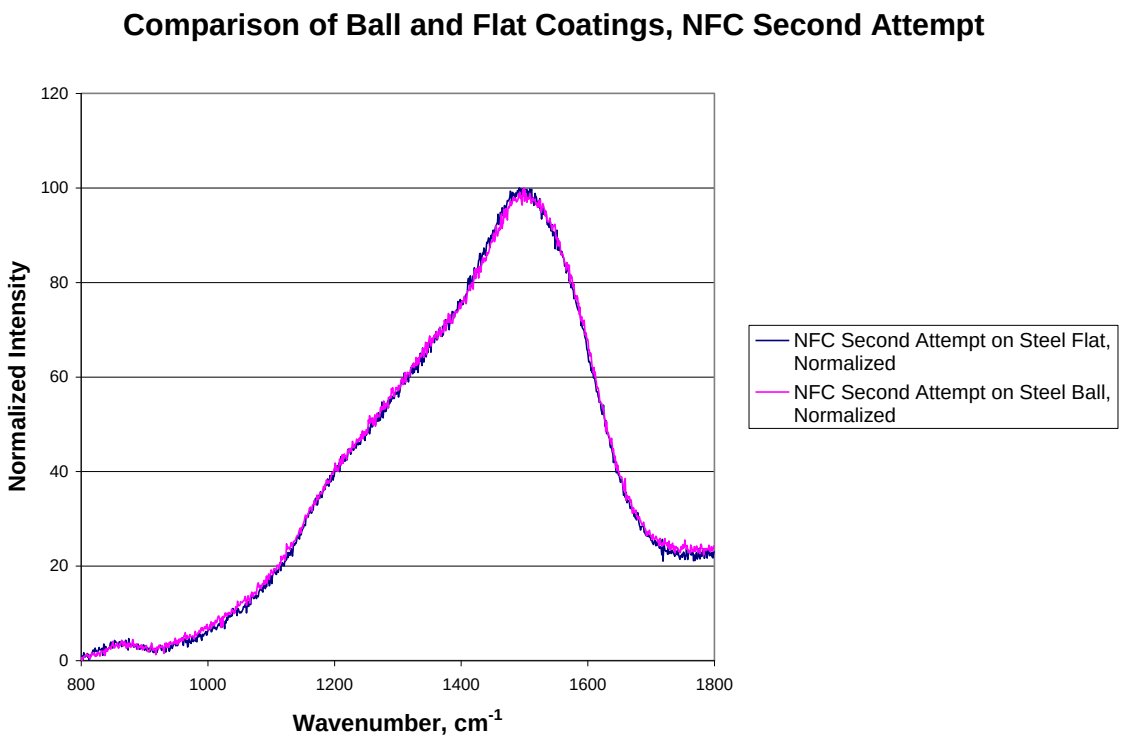
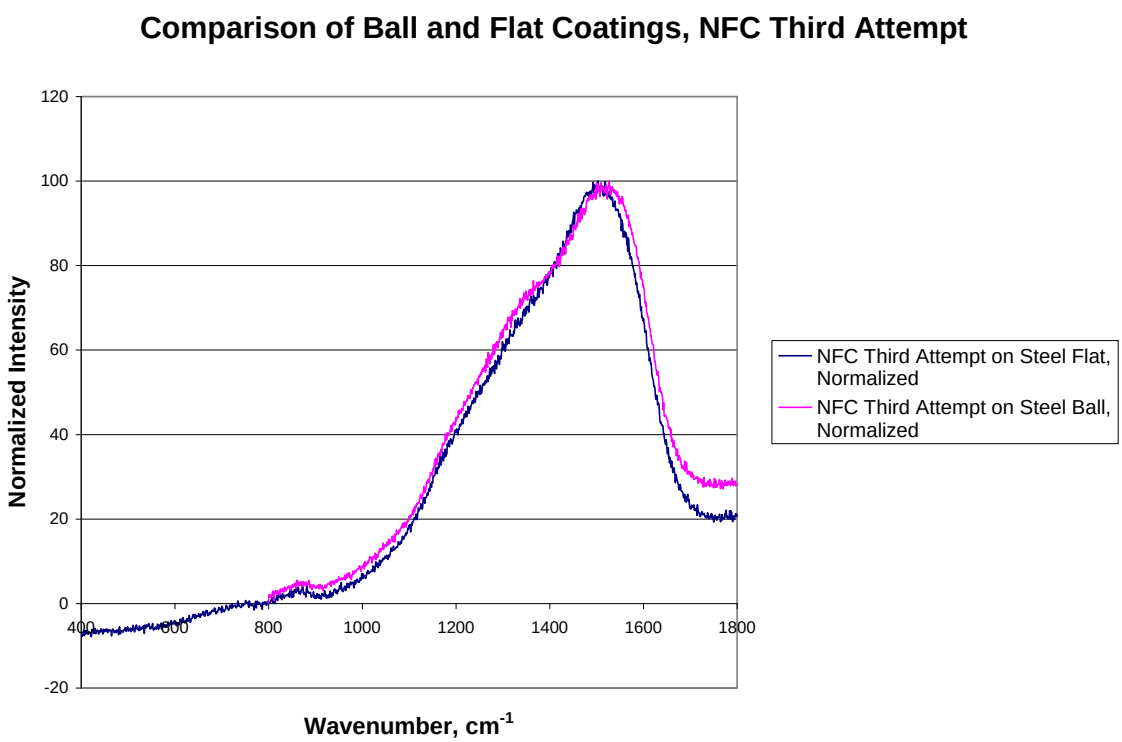


Figure 23: Raman spectra on the steel ball samples coated with the second and third attempts at NFC, normalized, together with spectra for diamond, pyrolytic graphite and NFC 6



(a)



(b)

Figure 24: Comparisons between the Raman spectra of steel balls and flats coated with the second attempt at NFC (a) and the third attempt at NFC (b), normalized