Evaluation of stability of monolayer injection molding tools coating

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ABSTRACT

We characterized stability of perfluorosilane based coating on Aluminum and Nickel prototype molds and mold inserts for injection molding (IM) polymer replication. X-Ray photoelectron spectroscopy (XPS) data, contact angles, surface energy and roughness data have been collected and used to assess stability and to predict coating lifetime. Metal tools have been characterized immediately after FDTS coating, and after 500 IM cycles. Contact angle data were measured for water, di-iodomethane and benzylalcohol. We observed detectable coating presence even after 500 IM cycles, as evidenced by Fluorine XPS signal and increased contact angle on all post IM samples. To conclude, we present controllable, covalently bonded mold coating, which is well suited for industrial application, coating that is reasonably durable, affordable, scalable to production, detectable on surface and especially suitable for rapid prototyping and mold geometry testing as well as methods to evaluate wear of such coating.

Keywords: perfluorodecyltrichlorosilane, injection mold, coating, demolding, polymer

1 INTRODUCTION

Injection molding (IM) process is probably the most widespread manufacturing process today. IM is used to make affordable everyday items as well as cutting edge microfluidic components, medical diagnostic devices and optical instruments. IM process engineers use prototype molds and mold inserts fabricated from Rapid Solidified Aluminum (RSA), especially for special mold applications in where quality is paramount, namely optics, photonics and microfludics. Simulation and mold prototypes are also used for verification of mold filling.

Another way to produce precise IM tools is combination of lithographic microfabrication on Si wafer and electroplating with Ni. Such process is usually called LIGA and is extensively used in microfluidic community [1].

Aluminum molds have substantially reduced lead time (days instead of weeks), lower manufacturing cost (30%) and excellent surface finish compared to steel molds. Aluminum surface roughness (RMS) is often below 5 nm after diamond machining. Ni inserts surfaces are limited only by semiconductor microfabrication processes and can easily reach nanometer range. To protect the mold, facilitate de-molding and improve surface of plastic parts one usually coats the mold. Unfortunately, conventional hard metal coating with thickness of few microns may ruin small features. Conventional coating deposition is also complicated, expensive and coating near impossible to repair.

We proposed perfluorinated trichloro-silane (FDTS) coating for both Nickel and Aluminum, realized it and tested coating stability in challenging conditions of real life injection molding, up to 200MPa and 280°C. This result is important for production of advanced plastic parts as it indicates what minimum guaranteed and total expected coating lifetime is, and when one does to have re-coat tools.

2 MATERIALS & METHODS

2.1 Metal Molds

Tested Aluminum mold insert was 3 mm thick and 65 mm wide disk from 6061 Aluminum alloy, covered with array of concave microlens cavities created by single point diamond turning. Tested Ni insert was 370 µm thick and 100 mm wide disc cut from commercial, highly polished Ni sheet.

2.2 Perfluorosilane coating

Mold surfaces have been processed in cleanroom, first cleaned in DI water, and then rinsed with acetone, isopropylalcohol and blow dried in dry nitrogen.

Perfluorodecyltrichlorosilane (FTDS) monolayer coatings were deposited using a commercial MVD 100 system from Applied Microstructures and multi-cycle recipe [2]. Precursor chemicals were heated to about 50°C while the sample was kept at approx. 35°C. Process was started by O_2 plasma with 200 sccm flow at 250 Watts power for 300 seconds. This cleans and primes the surface, and ensures that metal surfaces are coated with oxide. The main deposition cycle consist of 4 releases of FDTS at 0.5 Torr, 1 release of water vapor at 18 Torr and 900 seconds of reaction time. The cycle ends with 5 purge steps. The main

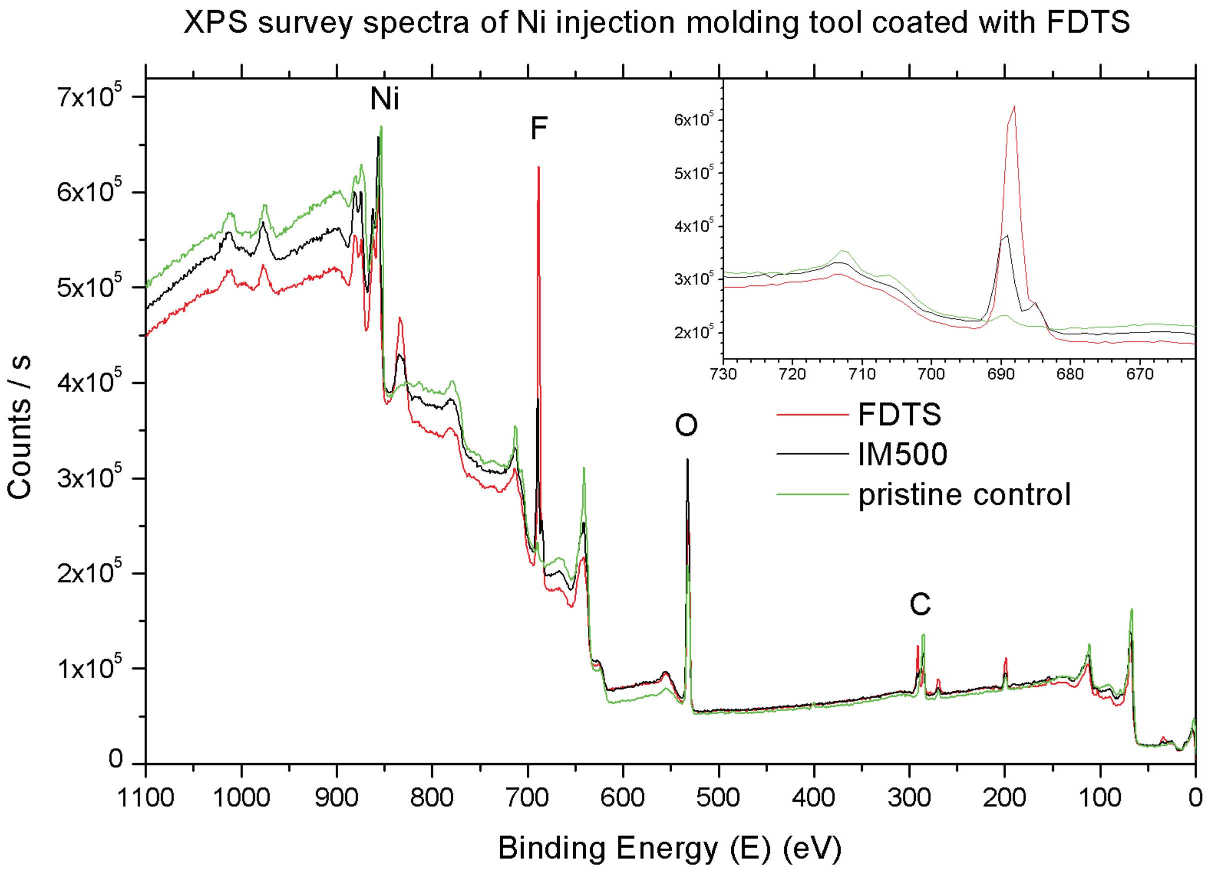

Figure 1. Ni XPS survey spectra with F peak insert.

cycle was repeated 4 times, resulting in total processing time of approximately 80 minutes.

2.3 Injection Molding

The Ni tool was tested using an Engel Victory 80/45 Tech IM machine. We performed more than 500 cycles, first 200 with clear COC TOPAS (grade 8007S-04) and cold (20-30 °C) tool. Polymer was plastified at 200 °C and injected at 250 °C. Another 300 cycles have been performed with clear COC TOPAS (grade 5013L-10) and mold heated to 100 °C. Plastification temperature was 250 °C and injection temperature was 280 °C.

Aluminum mold was tested in an Engel Victory 200/55 IM machine, again with more than 500 IM cycles. First we tested 300 cycles using clear Polystyrene (Total Petrochemicals) material, and cold mold (20 °C) with melt temperature 250 °C and subsequently more than 200 cycles with proprietary yellow ABS material, at elevated mold temperature (90 °C) and melt temperature 320-340°C.

As usual, few initial shots have been used to set-up part volume, injection speed and briefly optimize filling and packing of tested part for each mold and plastic material.

2.4 Characterization

Both tool surfaces (Al, Ni) have been characterized in their pristine state prior to coating, then after FDTS coating and then after 500 IM cycles.

Contact angle was measured using Krüss DSA 100S Drop Shape Analyzer at cleanroom. We used 3 liquids, namely benzylalcohol, diiodomethane and water to provide sufficient number of pairs for good calculation of surface energy. The shapes of sessile drops of liquid on sample surfaces have been extracted 10-12 times from each drop in 0.5 second interval, in first 6 seconds after deposition, with more than 5 good drops on each surface for each fluid.

Photoelectron spectroscopy (XPS) data have been collected using a Thermo K-Alpha system, manufactured by ThermoScientific, with the spot size at the instrument maximum (cca 400 microns). Samples were not tilted so takeoff angle was 90°. Survey scans energy range was 0-1350 eV, with a pass energy of 200 eV, 10 scans and collection time of approx. 660 seconds. Spectra have been collected on at least 2 spots on each sample, with spots at least 10 mm apart from each other to account for possible surface heterogeneity. Quantitative analysis of elemental composition from survey spectra and core levels deconvolution was done in the software package ThermoAdvantage version 4.75. Estimated relative error for elemental quantification is below 1.8%.

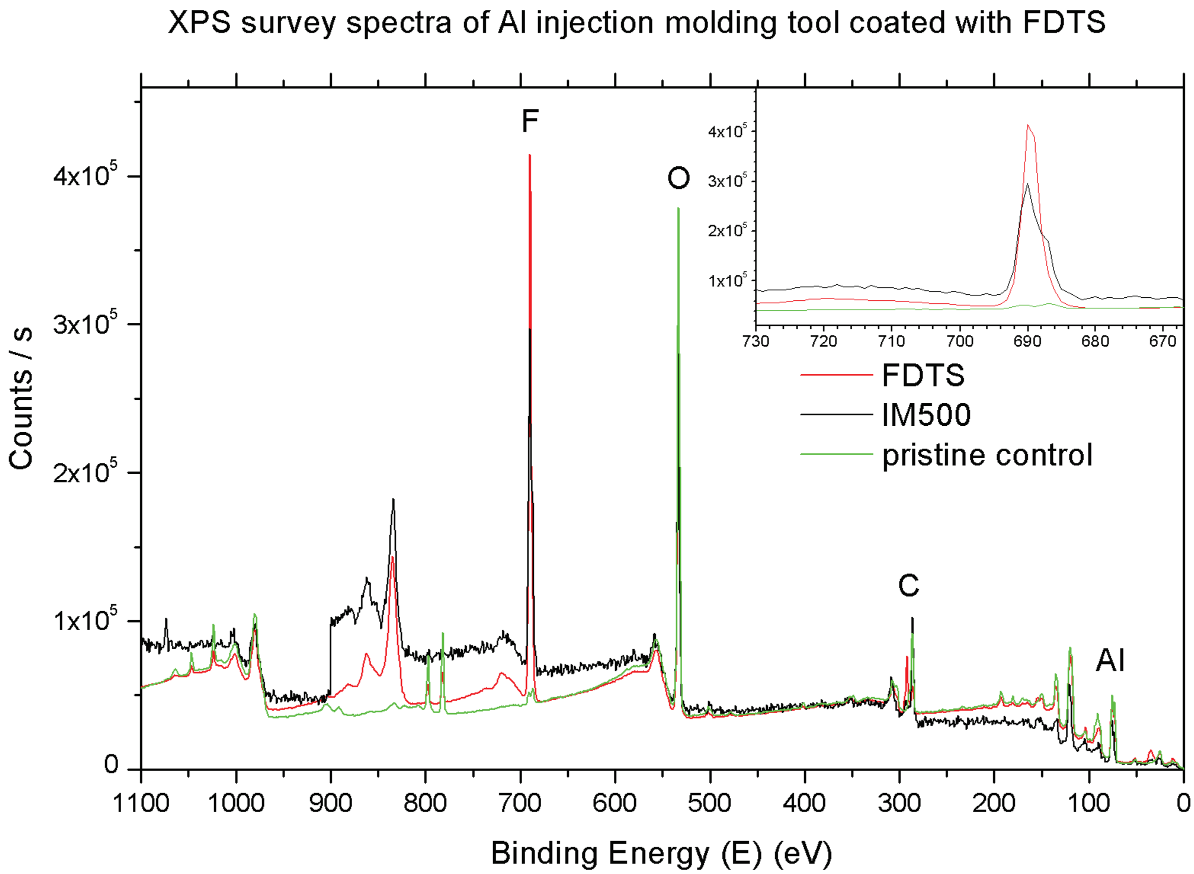

Figure 2. Al XPS survey spectra with F peak insert.

3 RESULTS

We compare samples coated with FDTS, same sample after more than 500 IM cycles and pristine sample to assess stability of coating. XPS survey spectra (Figures 1 and 2) shows main elements detected on sample surface. There is strong Fluorine peak near 690 eV [3]. We can see well detectable concentration of Fluorine even on post IM samples. This is clear evidence that coating prevails over 500 cycles as tested on both Ni and Al surface. Fluorine concentration decreased in comparison with freshly coated samples as one can intuitively expect. Fluorine concentration as effect of treatment is shown in Table 1.

Treatment	Nickel	Aluminum
FDTS Coated	36.5%	29.8%
Injection molded	20.5	27.6%
pristine	1.1%	0.9%

Table 1. Atomic percentage of Fluorine as detected by an XPS quantification.

Carbon 1s core spectra deconvolution on freshly coated sample shows 5 main peak components; most prominent are high binding energy (BE) peak components at 294.47 eV and 292.13 eV, with FWHM of 1.04 and 1.48 eV. Those high BE components can be attributed to functional –CF2– and –CF3 groups in an FDTS molecule. From the chemical structure of FDTS molecule can one anticipate ratio of those two components 7 and measured ratio was indeed 6.89. Other 3 less prominent peak components can be attributed to oxidized Carbon compounds, such as carbonyl and carboxyl groups. This result is in accord with reference literature [4]. Sessile drop contact angles have been plotted and analyzed and after removal of obvious outliers (irregularly shaped drops) have been reevaluated and shown as figures 3 and 4 for Nickel and Aluminum.

Extracted error weighted contact angle data have been used to calculate surface energies according to extended Fowkes and Wu methods [5] using fluid pairs. SE results are shown in Figure 5.

4 DISCUSSION

From XPS elemental quantification we can see that there is well detectable amount of fluorine atoms on all post IM samples. This is clear indication that at least some part of the coating did survived harsh conditions of thermal cycling, elevated pressure and temperature and polymer flow of the mold filling during injection molding. We can guarantee minimal coating lifetime to be at least 500 cycles, which might be fully sufficient for prototype mold or specialized devices.

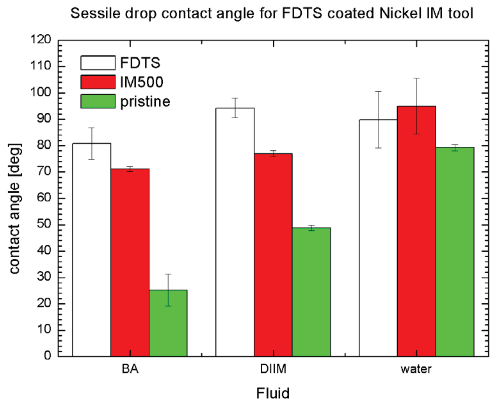

Figure 3. Drop contact angle on Ni using benzylalcohol, diiodomethane and water.

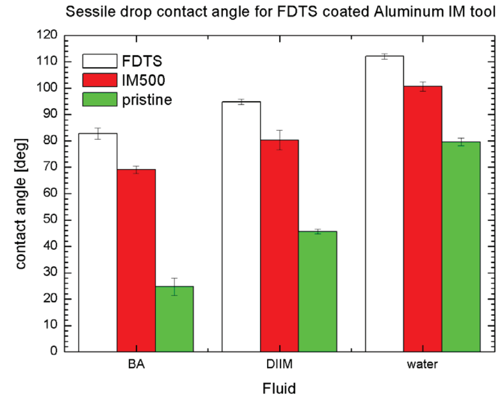

Figure 4. Drop contact angle on Al using benzylalcohol, diiodomethane and water.

If we analyze loss of fluorine, corresponding to loss of FDTS over first 500 cycles, one can see that there is much larger loss on Nickel than on Aluminum, 44% versus 7.6%. If we predict coating lifetime using linear extrapolation of loss, we can expect 1100 cycles for FDTS coated Nickel and 7700 cycles for Aluminum.

Surface energy data give somehow lower estimates, cca 2680 resp. 2550 cycles for Nickel if one uses Ext. Fowkes resp. Wu method for SE calculation. For Aluminum we get cca 2000 resp. 2800 cycles from SE data.

Since we expect coating loss to be non linear, we perceive lifetime from XPS to be more realistic. There are 2 reasons, upon brief characterization after first few shot we get CA data close to those at 500 cycles. Second, if there is removal of one monolayer at each cycle, one can expect coating to be fully removed after first few cycles, which apparently did not happen, supporting our hypothesis about non-linear rate of removal.

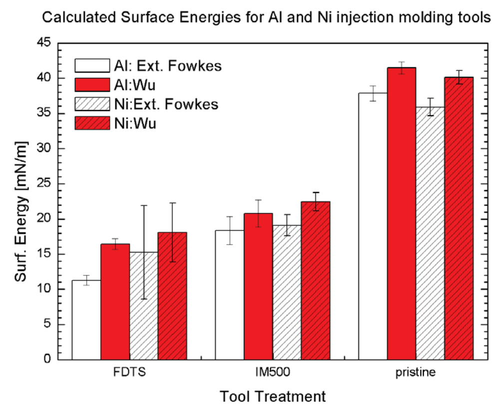

Figure 5. Surface energy plot for 2 calculation methods and both Ni and Al tool.

5 CONCLUSION

We detected fluorine and increased contact angle on post-IM samples and thus confirmed minimal FDTS coating lifetime of at least 500 IM cycles. This is true for both Ni and Al molds and both heated and cold mold. Analysis of the loss of fluorine (indicating loss of FDTS) shows relative loss of 44% on Ni and 7.6% on Al. Expected coating lifetime is 1100 cycles for Ni and 7700 cycles for Al. Therefore, FDTS coating on aluminum seems to be more wear resistant and thus Al is better substrate choice than Ni.

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