Slutrapportering av ÅF Projekt nr. 11-067: "Plasmabehandling och bearbetning av invändiga ytor"

Motivation till projektet och kort sammanfattning av projektresultaten

Målet med detta projekt var att utveckla plasmareaktiva processer vid substrattemperatur under 800 °C för bearbetning och behandling av invändiga substratytor och rörledningar med längder upp till 500 mm och en diameter mellan 20 och 5 mm.

Det bevisades att de aktiva plasma kan alstras inuti smala rör och hål. Lämplig plasmakälla för sådana ändamål utnyttjar principen av s.k. hålkatod. Det aktiva plasma alstrades inuti både ihåliga substrat med hjälp av patenterade plasmakällor utvecklade vid Uppsala Universitet. Plasma bearbetning inuti rören var möjligt vid både reducerade gastrycket och vid atmosfäriska och högre tryck. Erhölna resultaten och erfarenheter kommer att användas inom forlängningsfasen av projektet till ytterligare utveckling av isolerande beläggningar baserade på diamantliknande kol (DLC), särskilt för att skydda ytor av högspänningskomponenter.

Efter vissa modifieringar av de plasmakällor som utvecklats i projektet kan redan används även i andra FoU-verksamhet. Hybridplasmakällan är nu testas som en plasma-tändare och förstärkare i förbrännings lågor. Den ihåliga katodkälla skulle kunna användas för desinficering och kemiska reaktioner inuti vatten och vattenlösningar.

"Plasma processing and treatment of inner surfaces" - R&D results until December 2013

1. Short summary of the R&D carried out within the project

In accordance with the project proposal the R&D works have been directed to three important applications:

(1) Test depositions of hard films into steel tubes and components (e.g. forming tools, printing jets) at reduced gas pressure for higher ion energies - DEVELOPED.

(2) Pioneering tests of inner surface activation of metal pipes by the atmospheric plasma for enhanced adherence of corrosion protective inner paintings, or pretreatments for the PVD of films - DEVELOPED.

(3) Pioneering tests of PCVD of inside protective coatings at atmospheric pressure - DEVELOPED.

The activities included:
- The construction design and building of a new reactor for atmospheric pressure experiments.
- Design and development of the plasma sources for inside plasma treatments.
- The reduced pressure deposition of hard CrN films from Cr hollow cathodes (by PVD).
- The verification of feasibility of the atmospheric plasma treatment inside tube. Conference presentation and publication of the results.
- Surface analyses of the plasma treated and coated surfaces - utilization of special equipment.

2. Description of the results

Ad (1) - The depositions of hard CrN films have been tested in the nitrogen plasma generated by the radio frequency (13.56 MHz) and pulsed dc (0.5 µs, 250 kHz) power in the cylindrical Cr hollow cathode (6 mm o.d.) at reduced N_2 pressures selected between 0.1 Torr and 0.5 Torr (13 Pa - 67 Pa) in the reactor.

A 100 mm long linear slit type of the Cr hollow cathode has been tested, too. The cylindrical cathodes are suitable for depositions inside narrow pipes (≤ 20 mm), while linear slit cathodes can be used inside of the larger diameter tubing. The project work using linear cathodes were carried out with a part-time involvement of an external PhD student supported by one of our industry partners. Very high PVD rates of CrN films reaching up to 7 µm/min have been obtained in both arrangements. Nanohardness of CrN films was up to about 270 GPa. The Cr hollow cathode plasmas during deposition of CrN films is shown in Fig. 1. Some alternative applications of the hollow cathode methods could be promoted by the partner company Primateria AB in Uppsala.

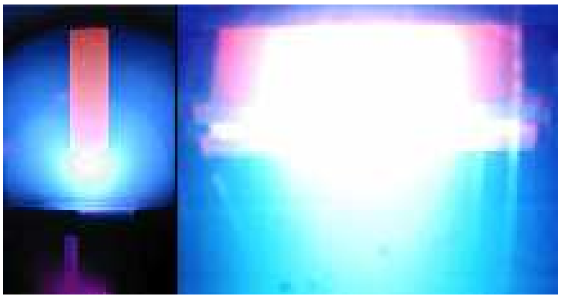

Fig. 1 Images of the hollow cathode plasma generated by the radio frequency power in cylindrical Cr cathode (left) and linear slit cathode (right). The working gas used in both systems was nitrogen, the gas pressure was 0.25 Torr. Cylindrical cathodes can be used for inside treatments.

There are numerous possibilities in altering the coating process. The process relevant to Fig. 1 is an arc-based large power reactive evaporation (PVD process) of Cr in nitrogen plasma resulting in hard CrN films. These films were referred already in the previous report from September 20, 2012. However, besides different cathode materials (e.g. Ti, Mo, Cu, Ni, or graphite, Si, Ge, etc.) there are also lower power chemical reaction processes (PE CVD) utilizing reactive gas precursors like CH4, C2H2, SiH_4, different oxysilanes, etc. which can be applied at very high coating rates of carbon, carbides, silicides, oxides, etc. The properties of resulting coatings (hardness, resistance, etc.) can be controlled by the process parameters (power, pressure, gas flow rate, mixing ratio of the precursor gas, etc.

Ad (2) – During 1st year a new test reactor with a hybrid plasma source (HYP) combining a microwave antenna discharge and a hollow cathode discharge has been build. This reactor with an air plasma at atmospheric pressure has been tested successfully, e.g. for inside treatments of brass pipes 12 mm i.d. and 2 mm thick wall. A simple demonstration of the plasma in a side window for planar test substrates is shown in Fig. 2.

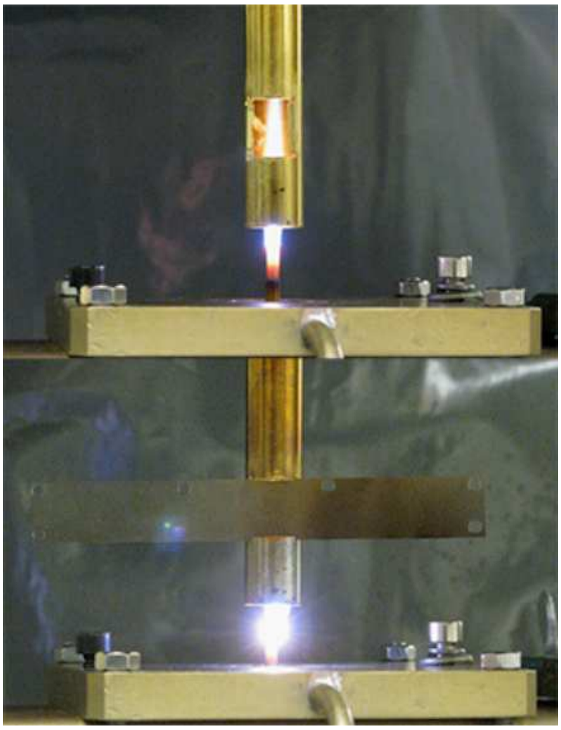

Fig. 2 The plasma plume generated by the HYP source before (top) and after (bottom) installing the planar test sample. It is evident that the plasma plume inside tube is not disturbed. Slight change after installing the substrate is probably caused by a change in the flowing air.

The plasma plume generated in air by the HYP source can be used for the inside treatment up and down within a quarter wavelength distance (about 3 cm) of the used microwaves.

During 2^{nd} year of the project a new version of the atmospheric plasma source based on s.c. Fused Hollow Cathode (FHC) was designed and built for inside tube treatments. The principle was shown already in the first project application. The plasma generated by this source (can be scaled both up and down) in argon gas is shown in Figure 3 for diameter 60 mm (treatment of larger cylinders). This source still needs some changes in its design to provide stable uniform plasma in air and other molecular gases. Recent experiments confirmed that this type of sources can be sized down and operated at very low short-pulsed DC power (≤ 20 W).

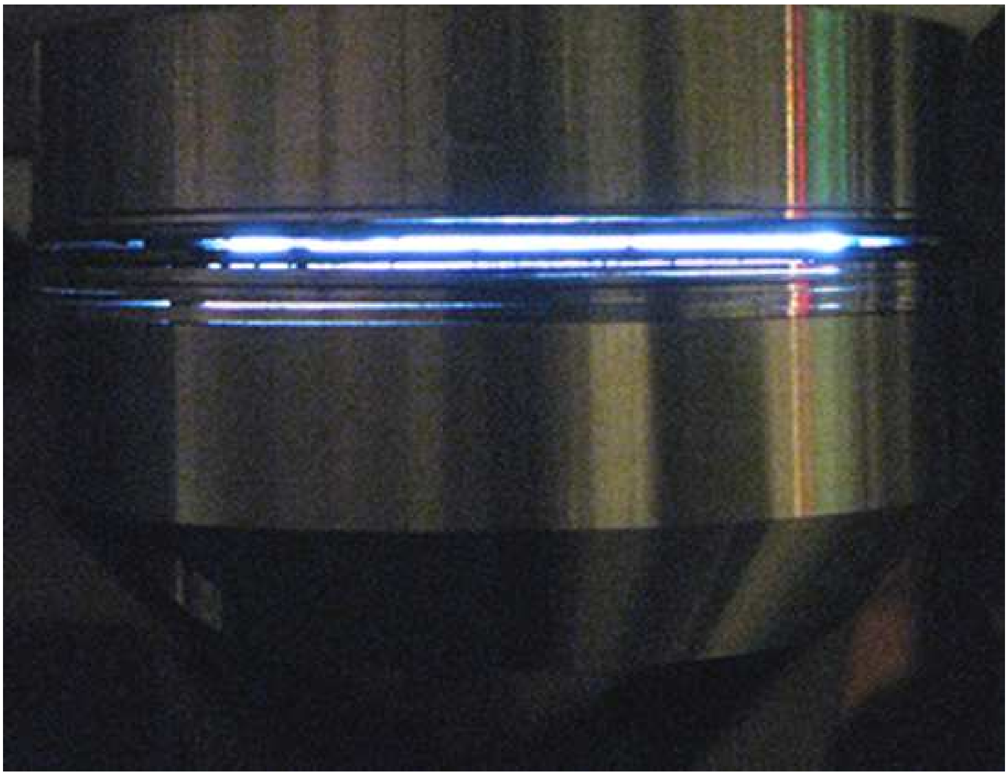

Fig. 3 Argon plasma generated by the FHC source with the RF power of 50 W. The source with outer diameter of 60 mm is applicable for plasma treatments inside hollow cylinders with inner diameter of 62 – 70 mm. Active precursors for PCVD can be mixed with the argon or supplied from outside the plasma. The source can be scaled both up and down.

Ad (3) - Pioneering tests of the PCVD of selected coatings using atmospheric pressure plasma have been carried out with hydrocarbon gas. For this purpose an original gas swirling feed system has been designed and fabricated. The system has been tested for inside tube PCVD of carbonaceous films using simple hydrocarbon precursors like LPG (Gasol) in air plasma alternatively in argon plasma. The whole concept is simple and can offer broad practical applications. Further development of the technology is anticipated mainly for diamond-like carbon coatings in the frame of extended phase of the present project. However, for certain applications where DLC coatings should provide extreme parameters like very high hardness or electric insulation, the subatmospheric plasma regimes with higher ion energies might be necessary.

3. Use of the budget approved for the project

The budget was used for building of experimental hardware and tests, as well as for the special diagnostics. The major part of the personal costs for the applicant has been so far covered from teaching and other projects. According to the agreed condition in the project, the assistance of the PhD student was not financed from the project funds. Several sources were used for this purpose: (i) from an external company, (ii) by EU stipendium ERASMUS, (iii) from internal funds of Division of Electricity. The PhD work will continue in the extended project phase.

4. Presentations of the Ångpanneföreningens Forskningsstiftelse

At the 55th Annual Technical Conference of the Society of Vacuum Coaters in Santa Clara (April 30 - May 3, 2012) the research support by the ***Ångpanneföreningens Forskningsstiftelse*** was highlighted both orally under the presentation and in written in the paper H-4 published in the SVC Proceedings (refereed). An oral acknowledgement was made also on October 2, 2012, after the presentation “Cold atmospheric plasma processing of inner surfaces” at Symposium of European Vacuum Coaters in Anzio, Italy, and on April 30, 2013 after the presentation “Atmospheric pressure plasma treatment inside hollow substrates. Forming solid carbonaceous deposits from CO_2” at ICMCTF in San Diego (presentation G3-1-5).

THANK YOU FOR YOUR SUPPORT OF OUR RESEARCH AND DEVELOPMENT!

L. Bardos, project responsible Uppsala, December 16, 2013