ION BEAMS FOR INDUSTRIAL SURFACE TREATMENT

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Abstract

- Since the late 1970s various approaches have been made world wide in order to establish ion implantation as an industrial surface treatment of metal components. However, the industrial application of ion-beam technologies (ion implantation) in the metal sector is still rather limited, and is restricted to relatively few niche areas. On the other hand other Plasma Surface Engineering (PSE) treatments like Physical Vapour Deposition (PVD) and plasma nitriding has become much more industrialized and is now used world wide on an large industrial scale

- The tutorial will focus on these facts and will not attempt to give a thorough and general review on industrial ion implantation. Instead, the tutorial will be focusing on one of the relatively few areas in the metal industry in which ion implantation has become a fully commercial surface treatment. Based on the authors 15 years of experience in industrialisation of plasma based surface treatments in Denmark where ion implantation in particular has played a major role, the presentation will attempt to analyse the scientific-, technical- and marketing factors governing the rather successful industrialisation of ion implantation in the Danish metal industry.

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History

- For many years it has been stated that the industrial use of ion implanted tools and components was prevented mainly by the high cost of the treatment
- Much effort has been put into developing ion implanters capable of producing very high ion beam currents. New high current ion implanters/ion sources and for instance PSII and PIII have been developed
- Thus, new technologies have been developed and much effort has put into the industrialisation of ion implantation.

History

- In the late 1980´s it was stated:
    - *'Now it seems that the application of ion beams to non-semiconductor purposes is ready for full-scale industrial exploitation' [Straede]*
- However, despite the optimistic forecast, commercialisation of the process was relatively moderate!
- Unlike the PVD (Physical Vapour Deposition), CVD (Chemical Vapour Deposition) and plasma nitriding techniques ion implantation has not succeeded in gaining a <u>vast</u> market, not even in the tooling trade where the technique have the largest potential.

History

- In the beginning of the 1990´s it was stated [Straede] , still optimistically but perhaps a little more reluctantly, that
  - *'Although a large number of technically successful improvements have been obtained by Ion Implantation, real commercial use of Ion Implantation for obtaining tribological improvements of tools and spare parts has emerged only in the last few years‘*
- However, progress was made and several examples of establishments/-companies which have applied/offered industrial ion implantation in the non-semiconductor area can be listed

History

- Examples of research facilities connected to commercial/industrial ion implantation (or trials) to some extent, some of which are more directly commercially oriented (list is not comprehensive):

  - *AEA Industrial Technology, TecVac and Tech-Ni-Plant (All UK)*
  - *MAT and Rossendorf (both Germany)*
  - *Nitruvid and IBS (both France)*
  - *INASMET and AIN (both Spain)*
  - *DTI Tribology Centre, Unimerco and CemeCon Scandinavia (Denmark)*
  - *Naval research Laboratory, Sandia Lab., Soutwest Research Institute, Los Alamos Scientific Lab., Army Research Lab, Corpus Christy Army Depot, Implant Sciences Corporation, Spire Corporation (USA)*
  - *Yutek (Turkey)*
  - *Matsushita Electric (Japan)*
  - *Beijing Normal University (China)*
  - *Australian Nuclear Science and Technology Organisation (Australia)*
  - *........Others!*

Status

- Many of these do not perform industrial ion implantation any more. Others than listed may have emerged on the market

- At present it may be concluded that the amount of industrial ion implantation facilities in the non-semiconductor field is <u>very</u> limited!

Status

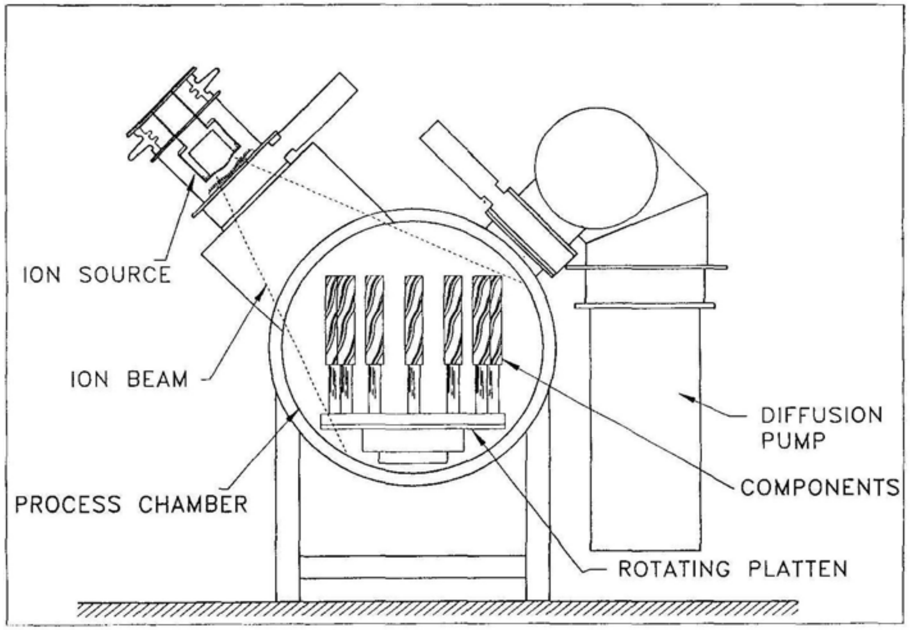
- In Denmark the situation seems to be rather opposite to this
- The commercialisation of ion implantation has been a relatively large success compared to many other countries
- The reasons for the relatively large success in Denmark is worth to analyse

The industrial Ion Implanter

- **Modified semiconductor machines**
  - Ion source + magnetic mass-separator + post acceleration + electrostatic beam steering + end-station/ target-chamber
  - Few mA beam-current normally de-focussed (broad beam) for non-semiconductor jobs
- **Highly efficient Ion sources for non-mass analyzed broad beams**
  - Ion source + end-station/target chamber
  - Gaseous and/or metal ions
  - Broad beams
  - 20 – 50 mA or even more
- **Plasma immersion ion implantation PIII/PSII**
  - End station = ion source
  - Immersion = no line of sight process
- **Selected area ion implantation (SAII). Machines dedicated for SAII industrial jobs**
  - Ion source + magnetic mass-separator + post acceleration + magnetically beam steering + end-station/ target-chamber.
  - 1- 10 mA beam-current. Focused and x- y scanned beam. Computer controlled beam and manipulator steering for non-semiconductor jobs

Broad beam machine (Implant Sciences Corp)

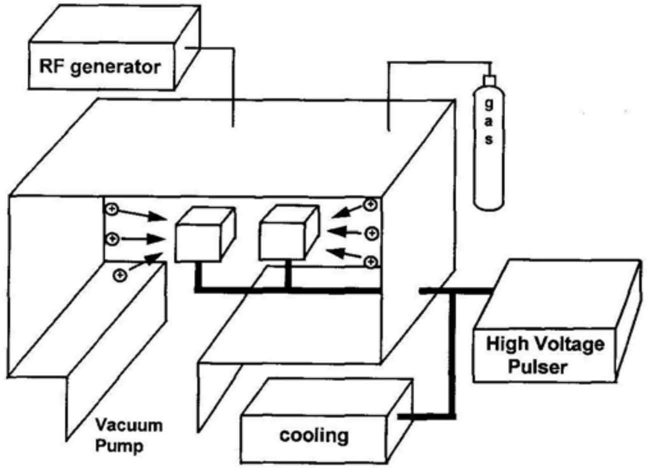
- **Non-mass analyzed broad beam implantation**



[Implant Sciences Corp, USA]

PSII machine (Los Alomos Nat. Lab)

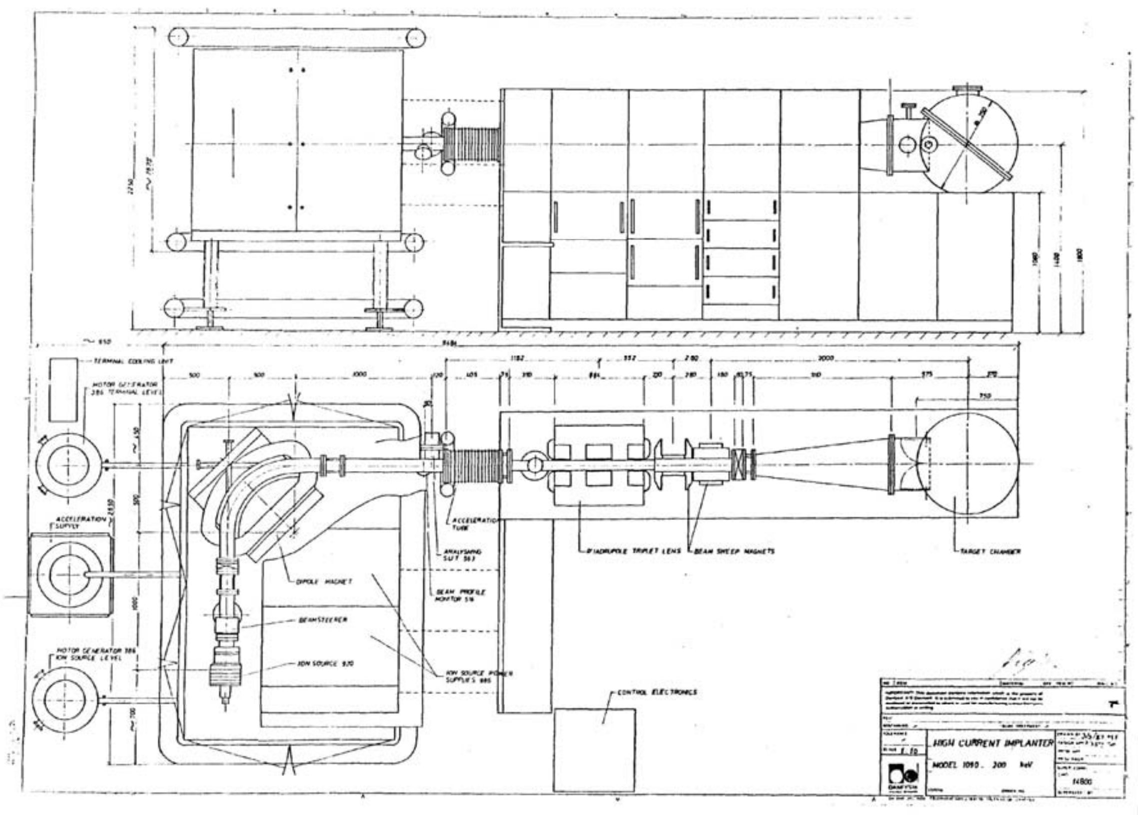
- PSII/PIII



- In PSII positive ions are extracted from the plasma by the high voltage pulses applied to the target. Ions impact almost all surfaces of the target

[C. Munson et al, Los Alomos Nat. Lab.]

SAII machine dedicated for industrial jobs. (Danfysik 1090)



Examples of machines used for non-semiconductor applications

An overview of machines (100–200 kV) used for production implantation into metals

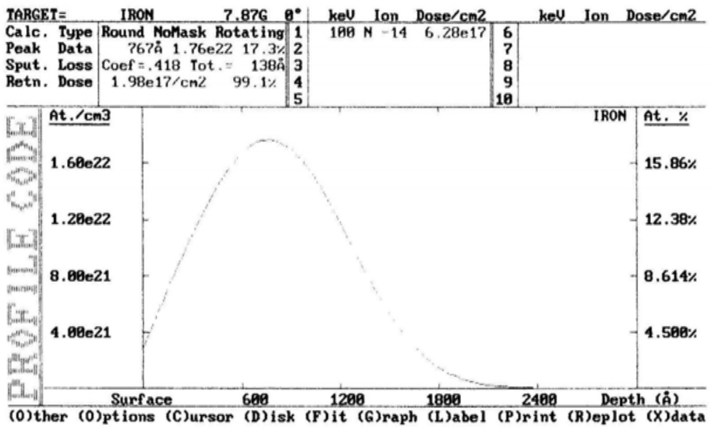
	Non-mass analysed with nitrogen source	Non-mass analysed with metal vapour vacuum arc source	Mass analysed, semiconductor type; refurbished	Mass analysed, metal type with magnetic scanning	PSII
Advantages	Simple operation. Compact.	Simple metal beam production. Multi energy implant. Compact. Easy to change ion species.	Relatively low initial investment. Process parameter control (at low current).	Process parameter control. Large areas and components. More than one end-station. Versatile. Selected area implantation.	Not line-of-sight. Simple. No target manipulation.
Disadvantages/ problems	Line-of-sight. Only nitrogen beam. N^+/N_2^+ mix.	No pure gas beam. Line-of-sight. Multi energy implant. Metallic droplets.	Space charge effects (at high currents). Line-of-sight. End station. Beam current limitations. Not all elements may be available.	Line-of-sight. Large foot print. Complex.	Scale-up problems. Secondary electrons. Cooling of many small workpieces. No local treatment possible.
Examples of commercial suppliers	Tecvac. Zymet. ISC.	ISM.	Eaton. Varian. Spire.	Danfysik. Whickham.	

- [B. Torp et al; Danfysik]

Mechanism of N implantation in short

- It is generally accepted that Cr –containing steel can be improved with respect to wear properties by implanting nitrogen

- Typically implantation parameters are in the order of:
  - 1 – 5 x10^{17} N/cm^2, 100 keV N^+

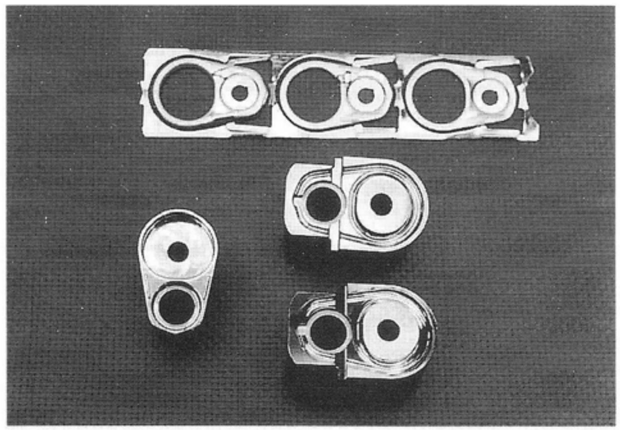


- Simulation [Profile Code] showing implantation depht profile and retained dose resulting from subjecting a rotating steel cylinder perpendicular to 100 keV N^+ at a total dose of (π) x 2 x10^{17} N/cm^2 with no mask. Thus corresponding to an implanting dose of 2 x10^{17} N/cm^2

Mechanism of N implantation in short

- Thus, industrial N implantation interacts typically with about 0.25 um of the steel and with a max atomic N concentration of about 15 – 40 %.
- This is obtainable at room temperature - much higher N concentration when compared to the equilibrium solubility of nitrogen in iron at room temperature
- Nitride formations. Excess N will precipitate at dislocations and at solute sites
- Strain obtained by nano sized nitrides and movement of dislocations are pinned by precipitations
- To some extent similar to nitriding processes – however these are made at equilibrium conditions (400 – 600 ºC)
- Result: Steel hardening (abrasive wear resistance) and passivation (adhesive wear resistance)

■ Example of critical steel tools improved by N-ion implantation

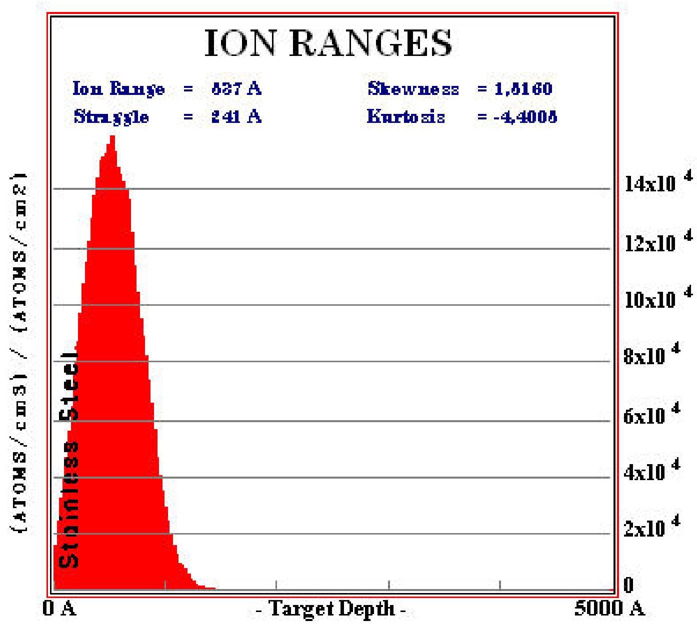


[INASMET and AIN, Spain]

Mechanism of Cr implantation in short

- Steel surfaces can be alloyed with Cr by implanting high dose Cr. Like stainless steels a Cr concentration of 18 – 40 % is desirable

- Typically implantation parameters are in the order of:
  - 1 – 5 x10^{17} Cr/cm^2, 150 keV Cr^+
  - For low doses (2 – 4 x10^{16} Cr/cm^2, 150 keV Cr^+) we get depth profiles like



(SRIM)

Mechanism of Cr implantation in short

- However, contrary to N implantation the surface sputtering from the Cr bombardment is significant. Sputter yields (Y) exceeding 5 is easily obtained.
- The steel surface exhibit inward migration due to the Cr bombardment ”eating” the implanted Cr profile.
- A retained saturation dose is obtained with max concentration (C) of approx.: C= [Fe atomic density]/Y.
- Thus max Cr concentrations exceeding 15- 20 % are normally not obtainable (saturation dose at about 1- 2 x10^{17} Cr/cm^2, 150 keV Cr^+)
- However, exhibiting the surface continuously with O_2 “feeds” the surface with atoms for the sputter erosion. In addition, the surface oxide is lowering the sputter yield.
- Thus, implanting Cr in low pressure O_2 atmosphere enables up to 40 % Cr concentration resulting in corrosion resistant steel surfaces.

Beam current is money! Or is it?

- For a given implanted area (A), dose (D) and beam current (I) the total implantation time (t) is:

$$t\ [\text{sec}] = D\ [\text{cm}^{-2}]\ \times\ A\ [\text{cm}^{2}]\ \times\ 1.602\ \times\ 10^{-16}[\text{C}]/I\ [\text{mA}]$$

- Thus for A= 1500 cm^2 ; D = (π) x 4 x10^{17}/cm^2 we get the following implantation times (such batch size is about 1/3 of a typical PVD batch)

Ion current [mA]	Implantation time [hours]
2	42
4	21
8	11
16	5.3
32	2.6

Beam current is money! Or is it?

- An industrial ion implanter is like an industrial PVD equipment a large investment in the order of 500.000 – 1 mill euro.
- Investment comprising interest and depreciation, consumables, service and repair, manpower, rent, etc
- The implanter must be able to make a break-even turnover in the order of for instance 150 - 300 euro per running hour

Beam current is money! Or is it?

Ion current [mA]	Implantation time [hours]	Estimated cost of batch [euro]
2	42	8400
4	21	4200
8	11	2100
16	5.3	1050
32	2.6	525

- So we do the following:

  - Make an ion implanter with beam current of 16 - 32 mA!
  - Sell a lot of ion implantation at PVD prices
  - This would beat out PVD on the market?

- However, such high current broad beam approach has its limitations

Example broad beam aproach

- A batch of tools is implanted by using a broad stationary beam with a diameter of Ø $\approx$ 45 cm => Beam area would be about 1590 cm^2

- Rotation of the target/workpiece is needed (axis 45°from the beam direction)

- Net area to be implanted is 1590 cm^2 x π = 4995 cm^2

- The process time for such batches would be in the order of 50 - 150 hours for 1 mA of beam current

- If the process time is to be reduced to a few hours, (like many PVD processes), Beam currents >$\approx$25 mA.

- If a 100 keV and 25 mA ion beam is used, the total beam power would be 2.5 kW, and the power density would be 1.6 W per square cm perpendicular to the beam

- When using a broad beam, a very large part of the workpiece surface is sub-jected to the beam power => The total amount of power impact can be very high

- **Heat capacity:**
  - $T_2 - T_1$= [time x (total beam-power on target)]/[Mass x (Specific heat of steel)]
    => Much to little capacity!
- **Radiation:**
  - $T_2^4 - T_1^4$ = (beam-power density)/[(emissivity of steel) x (Stefan-Boltzmanns constant)]
    => Typical allowed beam power density of 0.05 W/cm^2 for 200ºC and 0.4W for 500ºC => Target gets hot
- **Heat conduction:**
  - $T_2 - T_1$= (beam-power density) x (thickness) /thermal conductivity
  - ⇒ The only way to cool. In practical heat sinks are very hard to get perfect => Thin flat targets/component => Max 2 W/cm^2. For normal geometries often less than 1 W/cm^2 for max 200ºC.

25 mA broad beam

- Workpieces perfectly mounted on a water-cooled holder (ideal thermal contact) =>T ≥ 300°C in many cases

- Real workpiece mounting => heating can get even more severe.

- The question is what to do. There seem to be four options:

1. The heating could be accepted if this would not compromise the properties of the tool and the surface treatment itself
2. The batch area could be expanded to for instance Ø 90 cm
3. The beam current could be lowered. This, however, would make the implantation expensive
4. The total power impact on the workpieces could be lowered by reducing the surface area of the workpiece subjected to the ion beam.

Option 1) (accept heating)

- Ion implantation is no longer cold process. It would not be used on the tools and components where it is known to have superior properties
- It would be introduced on a market where PVD, (P)CVD and plasma nitriding are known to have remarkable results and low market prices.

Option 2) (increasing the beam size and batch size)

- Ø 90 cm instead of Ø 45 cm => 0.4 W/cm2 instead of 1.6 W/cm2 (for 25 mA, 100 keV). For some batch set-ups it may be possible to establish a low temperature process. But for many setups beam heating would still be hard to avoid.
- The total process time would be 4 times the process time for the "high temperature" Ø 45 cm batch
- However, the Ø 90 cm batch could contain 4 times the number of workpieces. Thus, the cost per workpiece could be quite similar for the two batch modes
- This only applies if it is possible to utilize the large batch capacity by filling up the chamber with 4 times the number of workpieces compared with the small batch mode.
- Very large batch modes are only economically feasible if the process chamber is filled to its capacity in most cases.

- Option 3) (lowering the beam current)
  - Expensive treatment when compared to coating and nitriding. Not realistic.
- Option 4) (Reducing the implanted area on the workpieces)
  - Can be made at low temperatures, at low process times, and with flexible batch sizes, enabling a low-cost treatment.

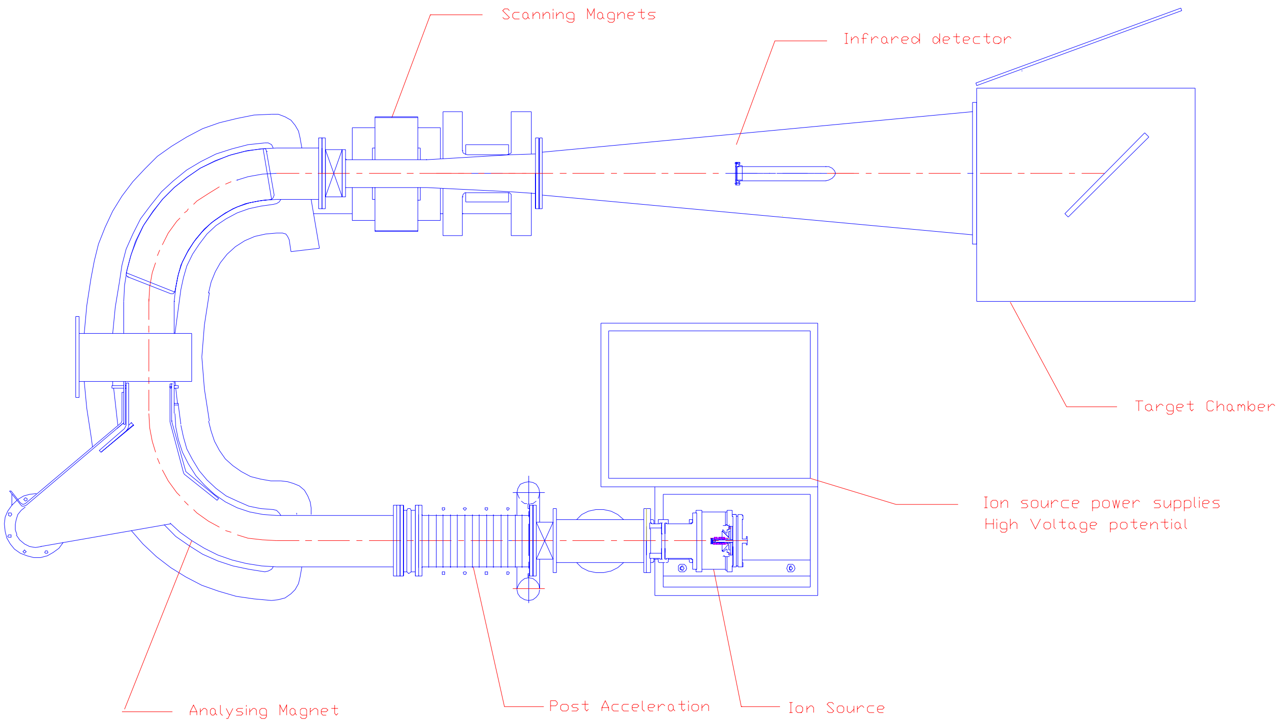
Selected Area Ion Implantation (SAII)

- In Denmark focus has been on another approach: Accurate ion beam steering. Performing ion implantation only on the relevant areas of the workpiece. The “Selected Area Ion Implantation (SAII) technique”.

- SAII reduces the implanted area and power impact by orders of magnitude when compared to a broad beam approach.

The Triion 1100 machine

- Simpler, more compact, 180 deg mass-separator with dipole adjustments
- Computerized interface and process control

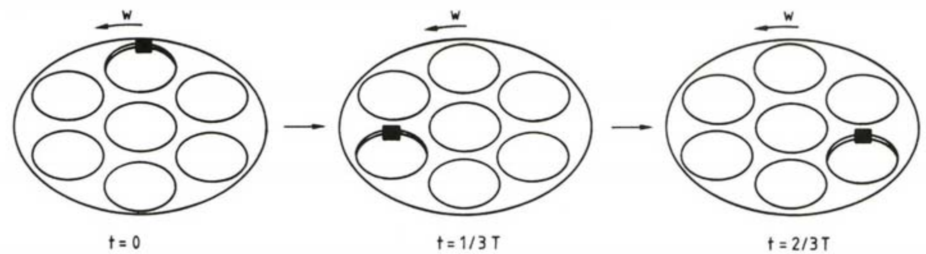


Example of SAII of tools

Rather large punches for thin sheet forming

- Such punches are subjected to mild abrasive and adhesive wear. They normally produce many hundred thousand items when unimplanted. Nitrogen ion implantation => several million items

  - Size Ø 20 cm. Critical area at the cutting edge-- is about 63 cm2 (to be optimally and homogeneously implanted
  - Beam diameter of about Ø 1 cm, horizontally fixed and scanned 1.8 cm in the vertical direction towards the centre of the critical area. Rotating tool. Axis held at 45° from vertical
  - 3 such tools can be mounted in one batch. PC programme controls the ion beam, enabling it to follow one tool and to shift frequently from tool to tool



- Area to be implanted is about 3 x 63 cm2 (homogeneously implanted) plus 3 x 88 cm2 (area of 'wasted beam'), in total 453 cm2.
- Beam current of 4 mA N^+ => process time would be about 1.5 - 3 hours
- Each tool is only subjected to about 100 W of beam power in average. Cooling the tools through the water-cooled tool manipulator is therefore easy, even with simple fixtures.
- If a similar batch has to be made by using a broad beam approach and with a similar low power impact, the process time would be more than 10 times longer.
- Or for a 40 mA broad beam approach we get the same process time (1.5 – 3 hours) but 500- 1000 W per tool
- The price of PVD coating of similar tools would be at least two times the price of the SAII, and in these cases nitrogen implantation has shown superior tribological properties when compared to coatings

Example of SAII of tools

- Injection moulds subjected to local corrosion

  - Many steel moulds used for injection moulding are subjected to local corrosion near the vents caused by the emission of aggressive gases from the plastics during the process

  - By chromium ion implantation corrosion can be prevented and tool life can be enhanced by 3 - 5 times

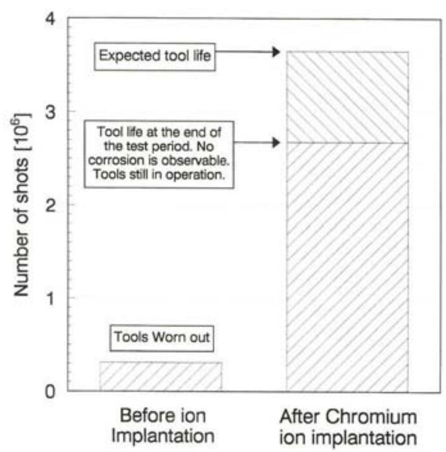
  - Dimensions: 10 cm x 30 cm x 30 cm. 12 vents are placed in a regular pattern. Each critical area of the vents is about 4 cm^2. The area to be optimally and homogeneously implanted is about 12 x 4 cm^2 = 48 cm^2

- Beam diameter is of about Ø 1 cm.

- Beam impact perpendicular to the surface and applying a horizontal and vertical beam scanning ((2 +1) x (2 +1) cm^2 =9 cm^2) over the critical area of each vent. Beam position shifting automatically between the 12 vents

- The implanted area is 108 cm2 in total (including the area of “wasted beam”)

- Process time is about one hour and no risk of unintentional heating



Comparison with coating techniques

a)

PVD
PVD <——————>
<——————>
CVD
Ion Impl.
PCVD
<——————>
——————>
<——————>

200°C 300°C 500°C 1000°C

b)

Ion Impl. PVD PCVD CVD

No influence on surface finish, tool shape and dimension.

Increasing influence on surface finish, tool

c)

Ion Impl. PVD PCVD CVD

Adhesive wear.
Mild abrasive wear.
Corrosion.

Adhesive wear.
More severe abrasive wear.
Corrosion (limited)

Severe abrasive wear.
Tools subjected to very large forces.

d)

Ion Impl. PVD PCVD PCVD CVD

Rather large punches/dies and draw dies for rather thin metal/steel sheet.

Plastic moulds.

Cutting tools for plastics, rubber, paper and meat.

Machining tools, drills, mills and inserts.

Rather small punches/-dies for sheet/plate in stainless steel.

Draw dies.

Parts of plastic moulds

Machining tools.
Inserts.

Deep drawing tools for sheet/plates

Typical niches for SAII

- Rather large, delicate, high-precision punches and forming tools for thin sheet forming
- Injection moulds
- Very sharp knives for paper, cardboard, plastics and meat

Status in Denmark

- Today, thousands of such tools and tool parts are ion implanted in Denmark each year
- CemeCon Scandinavia A/S is now operating a Triion 1100 machine in addition to three CemeCon unballanced magnetron PVD sputtering machines
- Ion implantation has become a large and integral part of the regular production at Cemecon Scandinavia A/S

Conclusions

- It is important to consider which kind of application niches broad beam, PSII and PIII techniques will have in the future

- If workpiece heating during the processes is inevitable, these techniques will to a great extent be in direct competition with well established PVD, (P)CVD and plasma nitriding techniques

Conclusions

- The SAII technique offers an alternative approach. It has been shown that by using the SAII a productivity gain of about ten times and a corresponding lower cost of ion implantation can be obtained

- However, this is only valid for those types of tools and components which are suited for this process

- By careful selection of the niche market for application of the SAII technique, it is possible to obtain a sound and regular market for commercial ion implantation in combination with coating services

Conclusions

- Thus, industrial ion implantation should be considered as an supplement to coating techniques
- Running a job coating business by using ion implantation only may be rather difficult

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