Application of DLC(diamond-like-carbon) coatings

-vacuum systems of TAMA and LCGT-

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1. Residual gas effect on the sensitivity
   direct measurement in TAMA
   required vacuum in LCGT
2. Ion pump lifetime and maintenance
3. Pressure distribution
4. Surface finish and modification
   duct surfaces and optical baffles
   outgassing rate measurements

1. Noise from the residual gas molecules

- **Optical path difference;**
  - **due to refractive index fluctuation**
  - **caused by pressure fluctuation**

$$\Delta L = \int_0^L \delta n(x')dx'$$

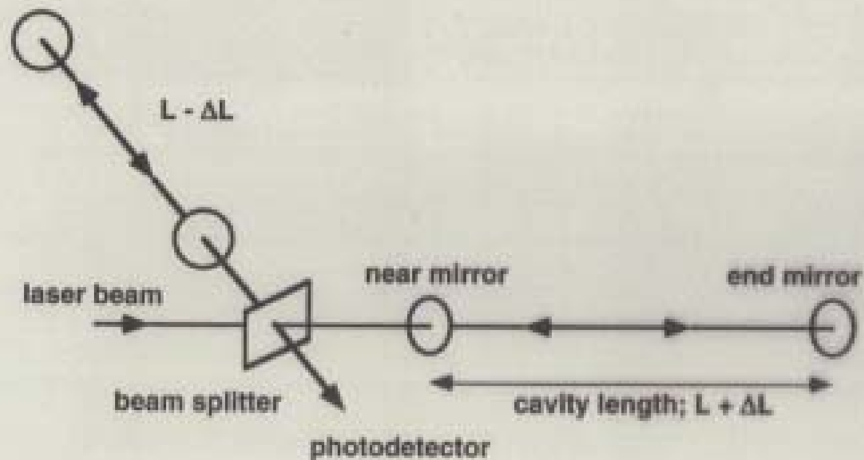
$$\frac{4\pi}{3}\frac{p}{k_B T}\alpha = \frac{n^2-1}{n^2+2}$$

$$\overline{(\Delta L)^2} = \overline{(Lh)^2} \propto \frac{(n_0-1)^2}{vL^{3/2}}p$$

$$\overline{(\Delta L)^2} = 4\sqrt{2}\pi\alpha^2 m^{1/2} k_B^{-3/2} \int_0^L \frac{p(x')T(x')^{-3/2}}{\omega(x')}dx'$$

n: refractive index
α : polarizability [m^3]
m: gas molecules mass [kg]
k_B: Boltzmann constant
ω : beam size [m]

Fabry-Perot-Michelson type interferometer



- **Direct measurement of ΔL in TAMA300;**

  * base level; 2×10^{-18} [m $Hz^{-1/2}$], @1 kHz (2000)
  * base pressure; 10^{-5} Pa (pump-off)
  * Xe gas introduction

gas	m	α	$\alpha m^{1/4}$
Xe	131	4.04	13.7
Kr	83.3	2.48	7.5
CO_2	44	2.59	6.7
H_2O	18	1.47	3.0
N_2	28	1.74	4.0
H_2	2	0.802	0.95

  - **The observed noise is proportional to the pressure.**

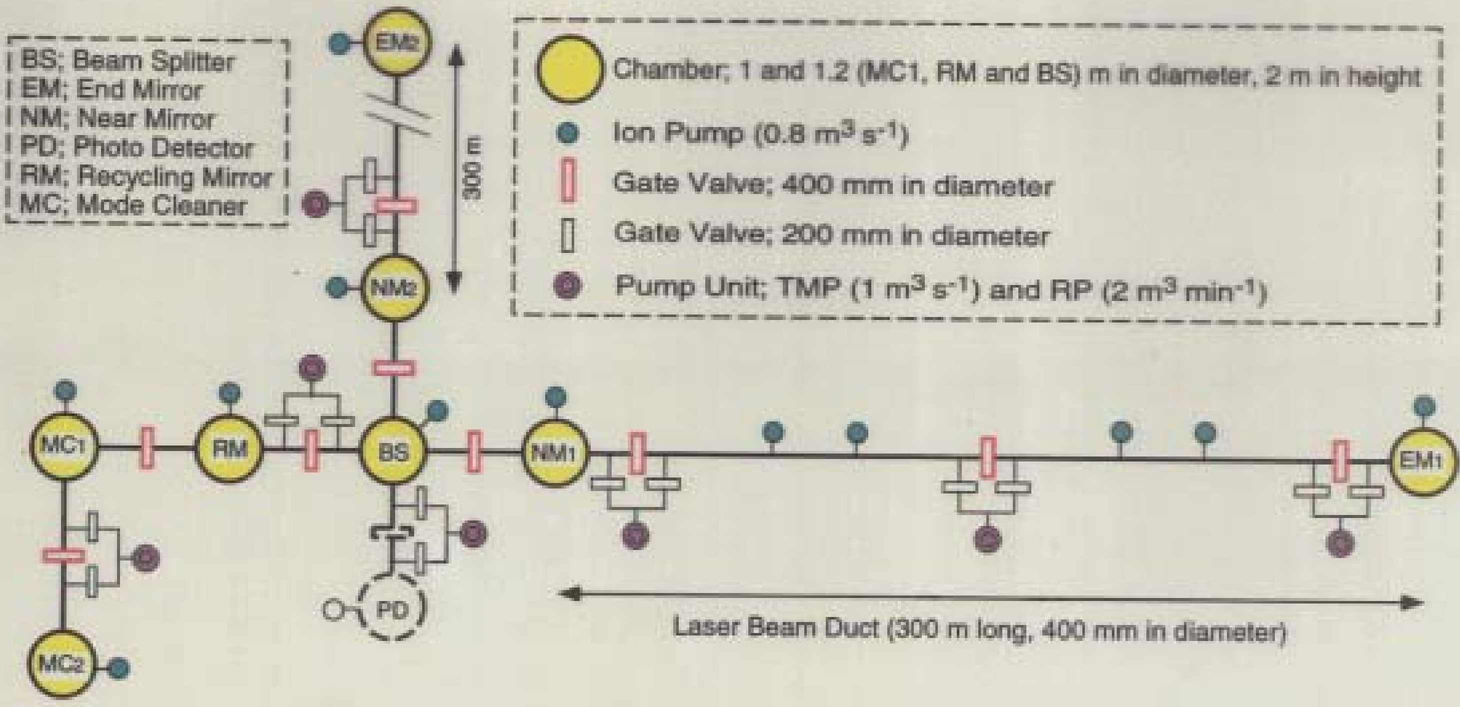
  - **The noise due to the Xe gas of 0.03 Pa corresponds to 2×10^{-18} [m $Hz^{-1/2}$].**

  - **The observed noise is consistent with a calculated optical path length fluctuation within a factor 2.**

- **Required vacuum pressure in the LCGT;**

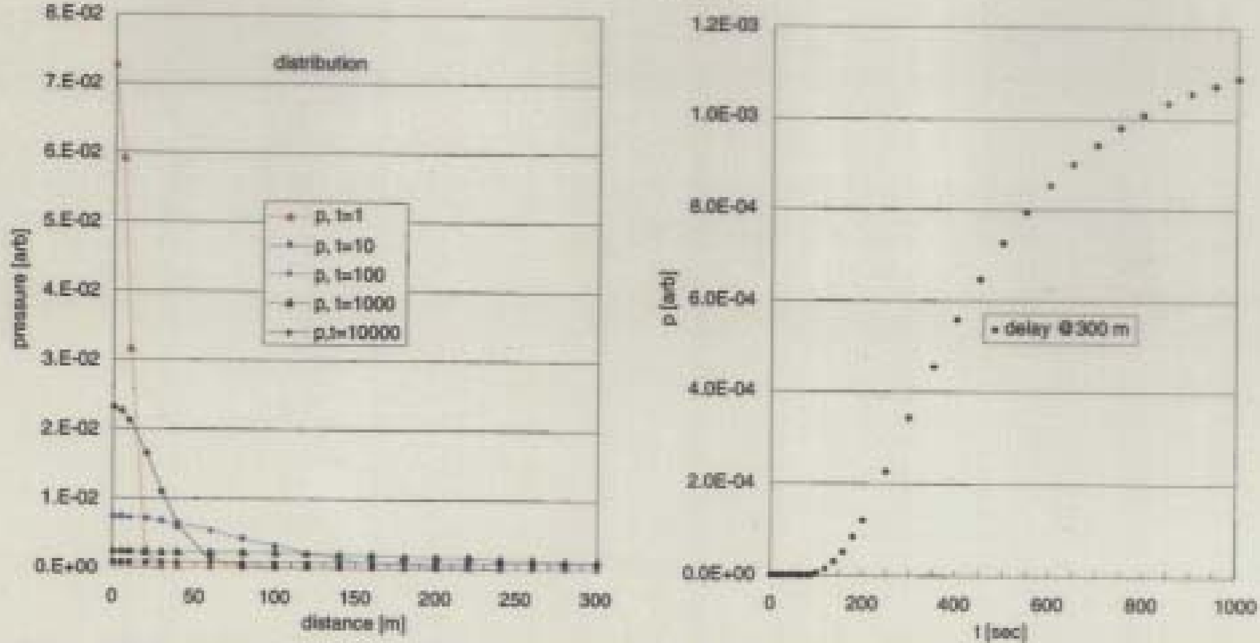
  - **2×10^{-7} Pa or lower for 1×10^{-20} [m $Hz^{-1/2}$].**

    * H_2O residuals dominant
    * with a safety factor of 10


BS; Beam Splitter
EM; End Mirror
NM; Near Mirror
PD; Photo Detector
RM; Recycling Mirror
MC; Mode Cleaner
Chamber; 1 and 1.2 (MC1, RM and BS) m in diameter, 2 m in height
Ion Pump (0.8 m3 s-1)
Gate Valve; 400 mm in diameter
Gate Valve; 200 mm in diameter
Pump Unit; TMP (1 m3 s-1) and RP (2 m3 min-1)
300 m
EM2
NM2
MC1
RM
BS
NM1
EM1
MC2
PD
Laser Beam Duct (300 m long, 400 mm in diameter)

$D\frac{\partial^2 p}{\partial x^2}=\frac{\partial p}{\partial t}$ において，$x=0$，$t=0$ で圧力がデルタ関数で与えられた場合（排気ポンプの無い無限に長いダクト）

$$p(t,x)=\frac{e^{-\frac{x^2}{4Dt}}}{\sqrt{2\pi Dt}}$$



$D=30\ m^2 s^{-1}$ ：直径 400 mm の円形断面ダクト内部の一端から Xe ガスを導入した場合に相当する（滞在時間 τ の影響は無視できる）

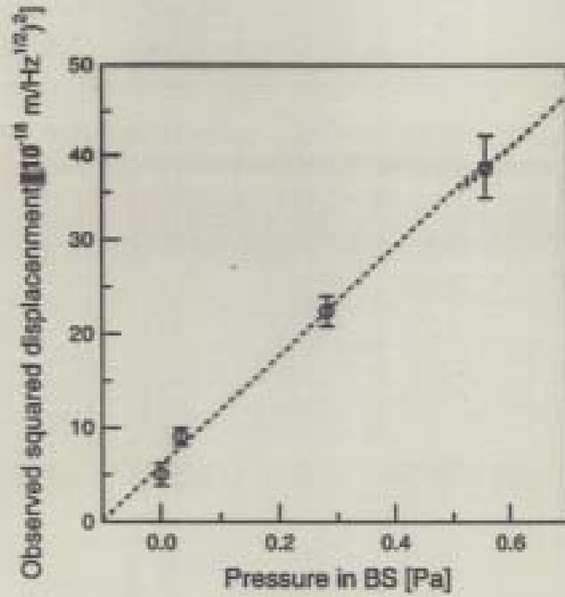


FIG. 3. Relation between the pressure in the BS chamber and the observed squared displacement noise. Measured points are indicated by circles with error bars.

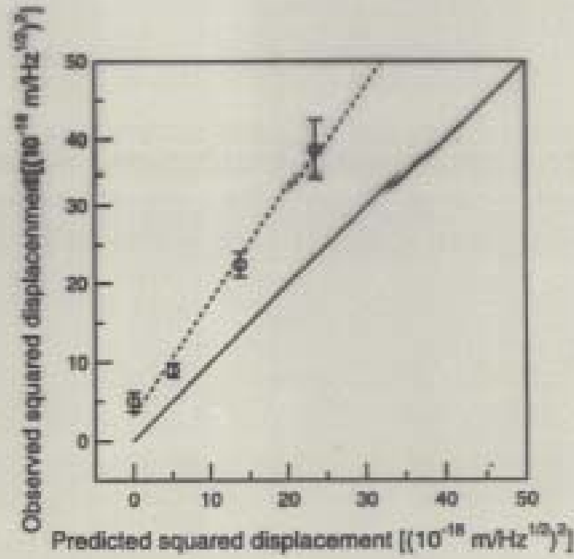


FIG. 4. Relation between the predicted and the measured squared displacement noise. The dashed line shows the fitting line, which has a slope of 1.5 and an offset of 3.2.

2. Ion pump lifetime and maintenance

- **cathode(Ti) dissipation**

  - 10^{-3} Pa $\times$ 5 10^{3} hrs = 5 Pa hrs

- **for stable operation**
  (without any pressure spikes/discharge)

  - 0.5 Pa hrs

    5 10^{6} hrs when operated at 10^{-7} Pa

- **maintenance(replacement) of ion pumps**

  - required number of replacement / year
    = (number of installed pumps)
    $\times$ (operation time for a year)
    $\div$ (lifetime of an ion pump)

* example (operated at 10^{-7} Pa);
number of installed pumps = 100
operation time for a year = 8.8 10^{3} hrs/year
lifetime of an ion pump = 5 10^{6} hrs

required number of replacement / year = 0.18

* TAMA300 (operated at 10^{-6} Pa);
number of installed pumps = 16
operation time for a year = 8.8 10^{3} hrs/year
lifetime of an ion pump = 5 10^{5} hrs

required number of replacement / year = 0.28

3. Pressure distribution

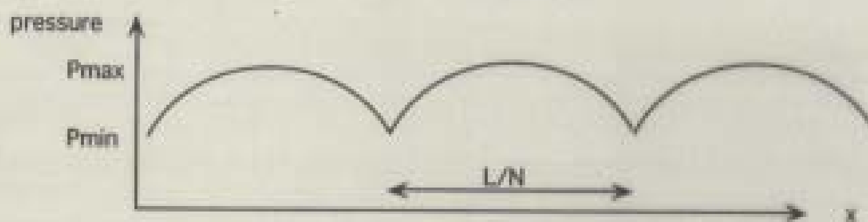
● in a long pipe

$$p(x) = -\frac{qAL}{2cN^2}\left(\frac{x}{L/N}\right)^2 + \frac{qAL}{2cN^2}\left(\frac{x}{L/N}\right) + \frac{qA}{SN}$$

* **assuming uniform outgassing rate from duct surface**

q; outgassing rate [Pa m^3 s^{-1} m^{-2}]
N; number of installed ion pumps
A; surface area [m^2]
c; conductance of the duct for unit length [m^3 s^{-1} m]
L/N: distance between ion pumps [m]
S; pumping speed of an ion pump [m^3 s^{-1}]

$$c = \frac{\pi D^2}{4}\frac{\bar{v}}{4}\frac{4D}{3}, \quad \bar{v} = \sqrt{\frac{8k_BT}{\pi m}}$$



● pressure distribution in the duct

$$k = \frac{p_{max}}{p_{min}} = \frac{SL}{8cN} + 1$$

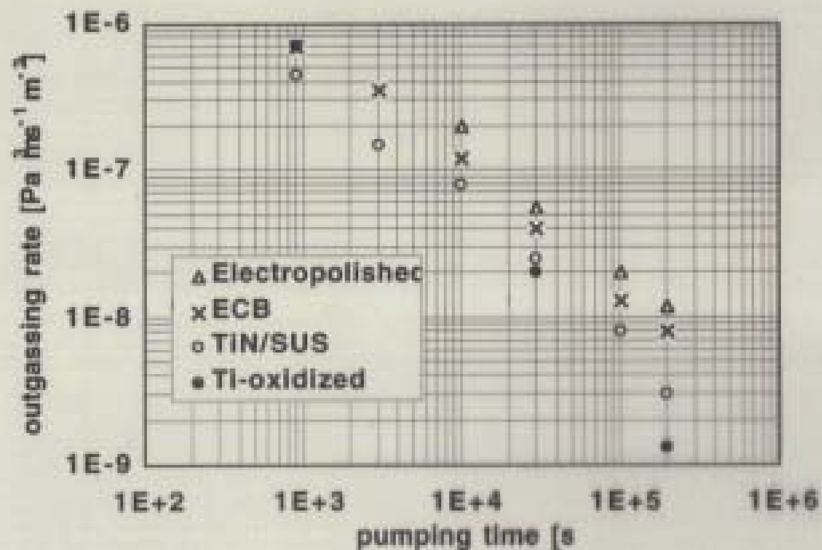
$$p_{min} = \frac{qA}{SN}$$

* **TAMA300;**
k = 2.0 (S = 0.8 m^3 s^{-1}, D = 0.4 m, L/N = 75 m)
p_{min} = 1.2 10^{-6} Pa (q = 10^{-8} [Pa m^3 s^{-1} m^{-2}])

* **LCGT;**
k = 2.0 (S = 1 m^3 s^{-1}, D = 0.9 m, L/N = 100 m)
p_{min} = 2.8 10^{-6} Pa (q = 10^{-8} [Pa m^3 s^{-1} m^{-2}])

4. Surface finish and modification

- **treatment for stainless steel**
  - **pre-baking (550C, 100h)**
    expected to reduce hydrogen content.
    only effective after dry-nitrogen exposure.
  - **TiN coating (1 µm, hollow-cathode discharge)**
    expected to be a barrier to hydrogen diffusion.
    effective for water molecules due to smoothness.
  - **electrochemical buffing, ECB (R_{max} < 0.4 µm)**
    expected to eliminate the surface degraded layer.
    effective due to smoothness,
    but not as passivated as TiN.
    the most advantageous (w/o furnace or liquid reservoir).
- **pure Ti with oxidized layer**
  effective, especially in lower pressure region.

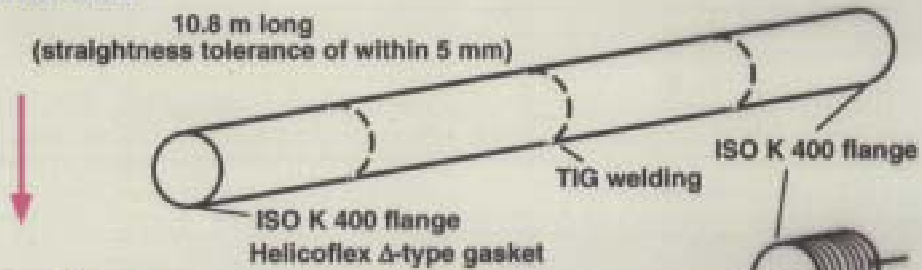


Outgassing rate of the test duct (1 m long, 150 mm in dia.), measured by a conductance modulation method.

ECB
Rmax < 0.4 μm
SS 304 (4 mm thick, 2.7 m long)

Forming
400 mm in diameter

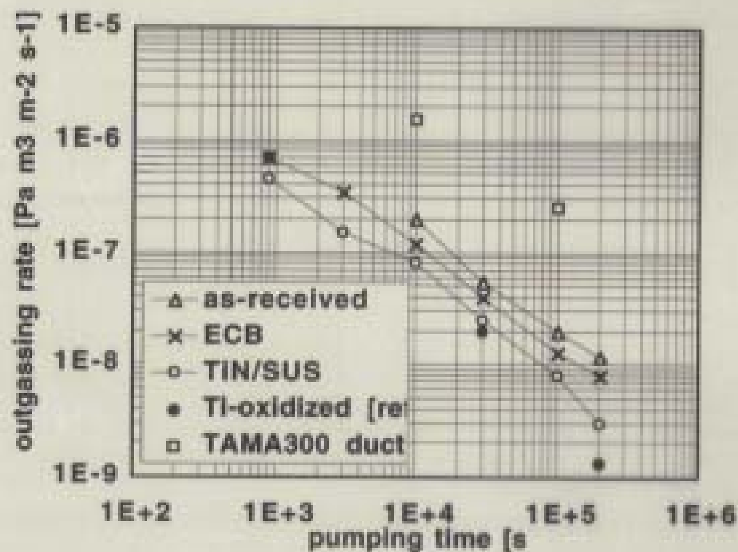
Welding
plasma arc welding
2.7 m long
ECB on weld beads


Unit duct
10.8 m long
(straightness tolerance of within 5 mm)
TIG welding
ISO K 400 flange
ISO K 400 flange
Helicoflex Δ-type gasket

Installing
SS bellows
(chemically polished
and vacuum fired)
V-shape holder
(aligned within + - 5 mm transverse offset for 300 m)

- outgassing rate in the TAMA300 ducts (ECB)

  - ~ 2.5×10^{-7} Pa m^3 m^{-2} s^{-1}; @10^5 s
  an order of magnitude higher than in test duct

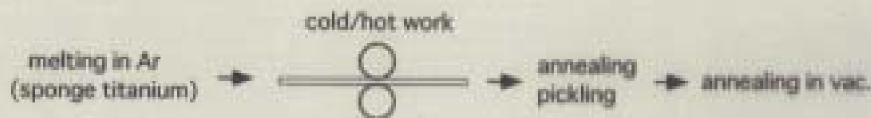


- possible explanation

  * higher contamination
    during manufacturing and/or transportation
  * no uniformity in surface coverage (H_2O)
  * higher pressure at the same pumping period
    (~10^{-5} Pa at 2×10^5 s; ~10^{-7} in test duct)
    smaller pumping speed S, for larger area A
    (S/A ~ 0.02; ~0.43 in test duct)

Titanium material

"as-received surface"



* not mechanically degraded
* natural oxide layer of 10 nm thick
* hydrogen contents of 50 ppm in the bulk
* low contamination

"heating process in controlled O_2"

* cleaning effect
* re-arrangement of oxide layer
  - →more passive for H_2O molecules than stainless steel oxide surface
  - →amorphous structure of 10 nm thick formed by 200C treatment
* too thick layer
  - →rutile structure, 100 nm thick, fragile

"dry process"

* w/o electrolytic solution (large reservoir)
* applicable for a duct (11 m-long, 0.9 m dia.)

"welding in inert gas"

clean beads

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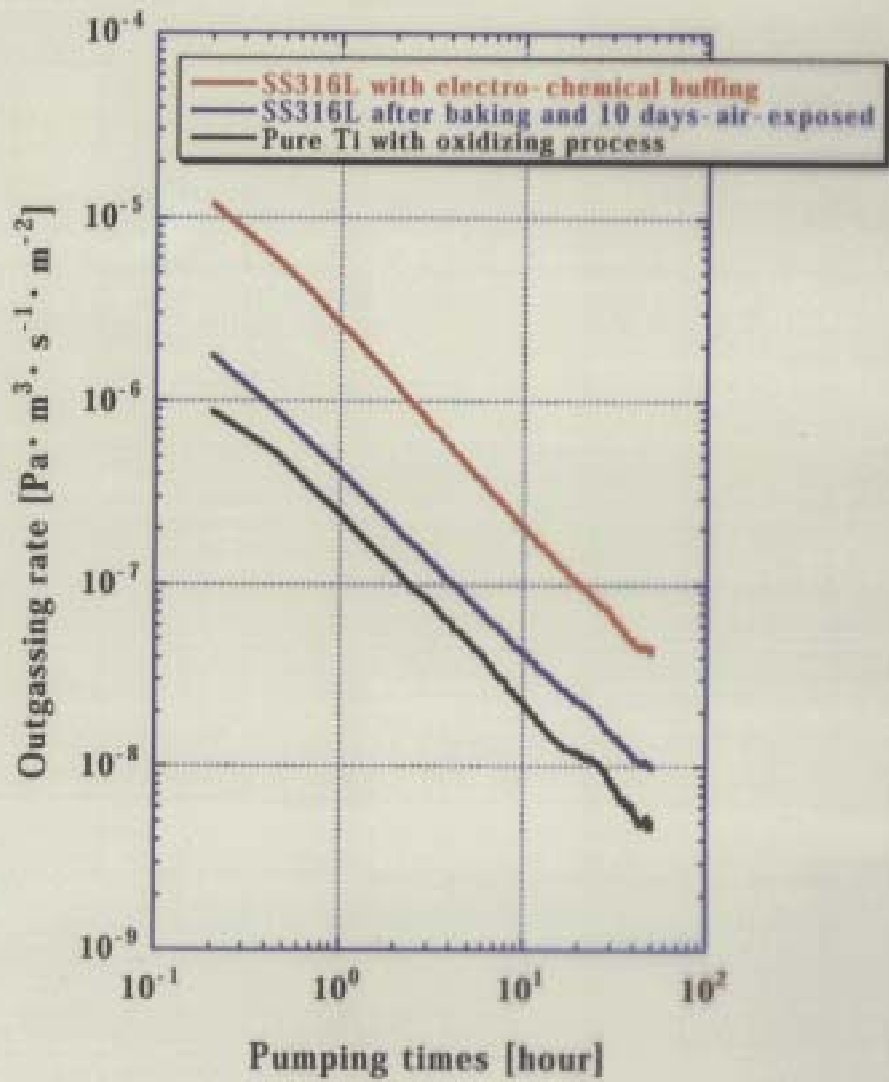
stainless steel

* chemical/mechanical/electrolytic polishing
  (for removing degraded surface)
* further heating process; pre-baking
  (for passivation)



SS316L with electro-chemical buffing
SS316L after baking and 10 days-air-exposed
Pure Ti with oxidizing process
Outgassing rate [Pa・m^{3}・s^{-1}・m^{-2}]
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-1}
10^{0}
10^{1}
10^{2}
Pumping times [hour]

Fig. 5　SEM image for pure titanium surface of MCP treated sample with oxidation at 450℃.

Fig. 6　TEM observation of cross section for pure titanium of MCP treated sample with oxidation at 200℃.

酸化処理したときのXPSによるデプスプロファイルをFig. 4に示す.

3.2　表面分析

真空特性を膜構造の面から評価する目的のために酸化膜構造に関する表面分析を行った. 本表面分析は表面の凹凸の影響を低減するためにERDAを除き, すべて純チタンJIS-2種の鏡面研磨のサンプルで行った.

Fig. 5に450℃で酸化処理したサンプルを折り曲げて撮ったSEM写真を示す. 表面の酸化膜の割れが観察でき, 脆い剥離しやすい膜質になっていることがわかる. 酸化膜の割れは200℃で酸化処理したサンプルでは認められなかった. Fig. 6に200℃で酸化処理したときのTEM写真を示す. XPSのデプスプロファイルで測定された値と同じ約10 nmの滑らかなほぼ均一な厚さの酸化膜が形成されている. 酸化処理無しのサンプルでは3～10 nmとやや不均一になっており, 酸化処理により膜厚が均等化されている. XRDの測定結果は, 酸化処理無しと200℃での酸化処理では酸化膜は結晶化しておらず, 450℃での酸化処理によって正方晶系でルチル型構造のTiO_2が形成されていることを示している. 450℃の酸化処理では結晶化した酸化膜が成長することで放出ガス量が多くなると考えられる. ERDAの測定は, 純チタンJIS-2種, チタン合金3-2.5, チタン合金15-3-3-3の3種類の材質に対して, それぞれ酸化処理無しと200℃での酸化処理を行ったサンプルで実施し, 表面近傍の水素濃度を求めた. 表面から20 nmまでの深さの範囲で測定したが, 水素濃度と放出ガス量の間にはおおよその相関関係があることがわかった. 例えば放出ガス量が最も少ない純チタンJIS-2種を200℃で酸化処理したものは, 水素濃度が他の条件のものよりも低くなっている. 水素濃度は表面が最も高く, 深さ6 nm程度までは減少し, それより深い部分での濃度変化は少ない.

今回酸化膜のバリアー効果については確認できなかったが, 膜構造が放出ガス量に大きな影響を与えることがわかった. 膜厚が均一で薄く, 緻密でかつ非晶質である酸化膜が低放出ガス量を得るために有効である. 今回採用した200℃での酸化処理は条件を満足する有効な表面処理法であると考える.

4. ま　と　め

酸化処理を行った純チタン, チタン合金の放出ガス量をコンダクタンス変調法によって測定した. さらに放出ガスに影響を与える酸化膜の構造を調べるためにTEM他の表面分析を実施した. 低い放出ガス量を得るためには比較的低温の200℃での酸化処理が有効であり, 本条件では酸化膜厚さが自然酸化膜厚さ以上にはほとんど成長せずに, かつ非晶質でガス放出の少ない膜特性となっていることが確認された.

〔文　　献〕

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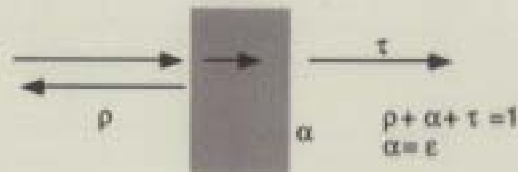
- Black surface for in-vacuum use as
  * baffles in the beam duct
  * supports of optical devices



- reflection coefficient of technical surface
  by Nd:YAG laser
  incident angle = 0 deg.
  detect. angle = 5 deg.

SS/ ECB finished	66%
Ti oxide surface	2% (with large diffusion)
SS/ TiN coated	72%
SS/ ECB+oxide	67%
SS/ DLC coated	11% (smooth surface)
Cu/ black Ni-P	0.2% (for wide range of λ)

- DLC→ formed by a "dry" process
- Black Ni-P→ formed by a "wet" process

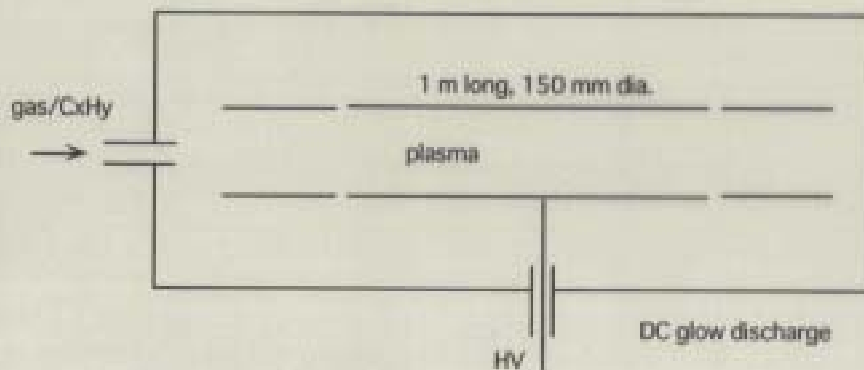
● DLC (diamond-like-carbon)

* amorphous structure
  graphite (sp^2) + diamond (sp^3)
  hydrogen terminated
  IR absorption (~ 7 µm)

* hard and smooth surface
  low friction-coefficient

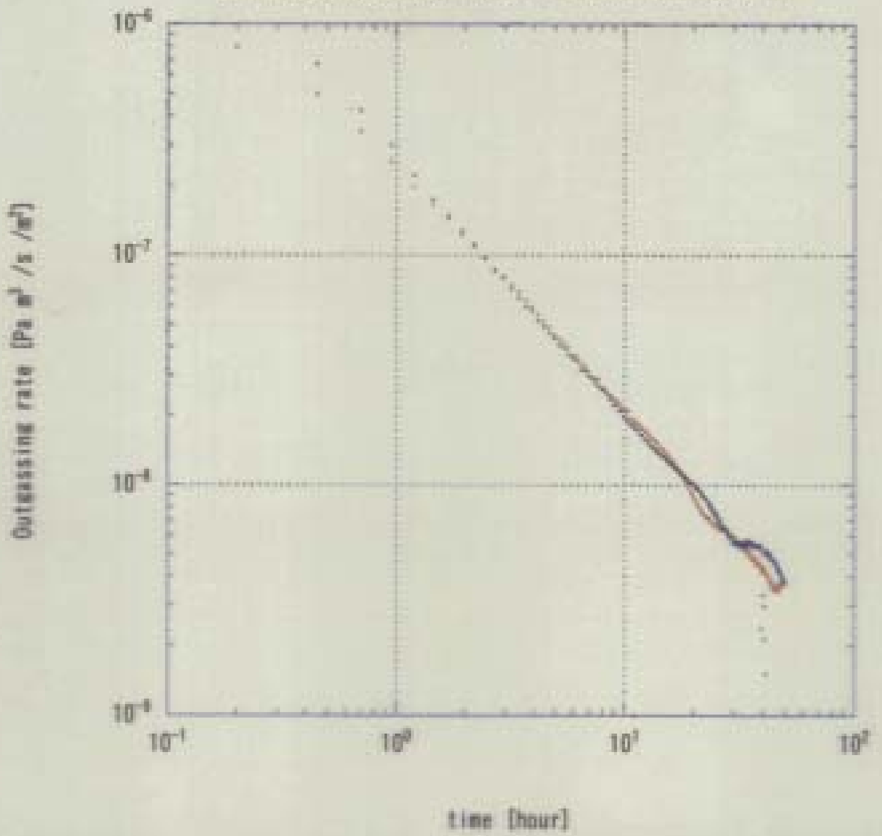
● coating technique

* Ion plating method
* Plasma CVD method (glow discharge)



* ECB/EP finished SS duct
* under layer of Si-C-O-H (0.1-0.5 µm thick)
* DLC film of 1 µm thick

● outgassing rate measurement
  (conductance-modulation method)
* low outgassing
* passive for H_2O molecules



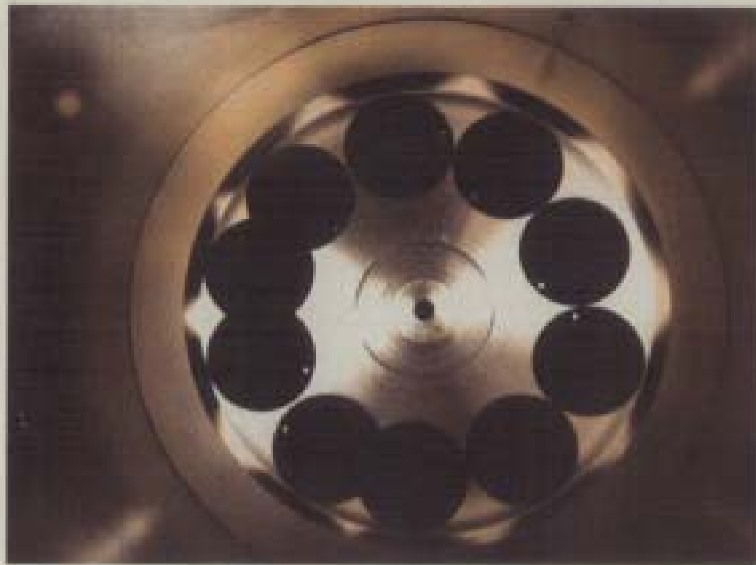
電解複合研磨にDLC 2002.12.04排気
電解研磨にDLC 2003.01.28排気
DLC coated SUS304 duct (φ155 × L1000 mm)
Outgassing rate [Pa m³/s /m²]
time [hour]

Black Ni-P

forming method

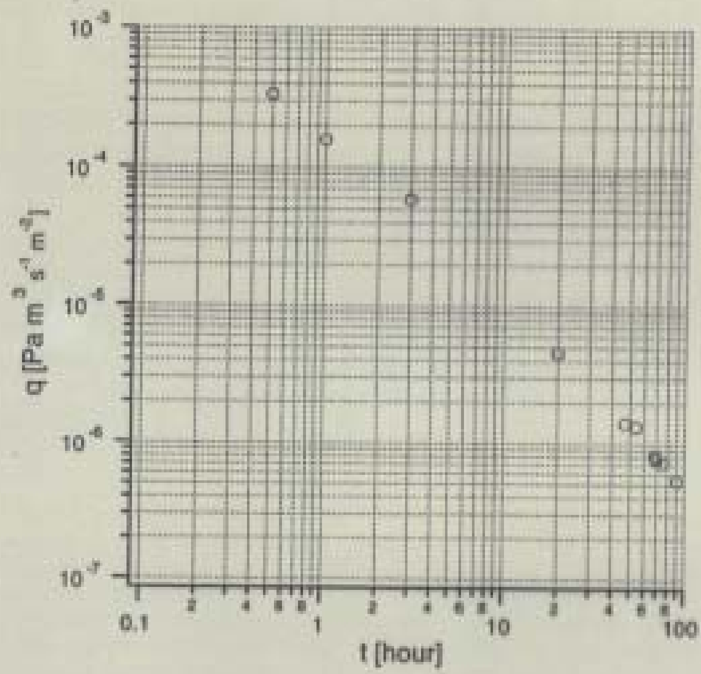
* electroless (chemical) plating of Ni-P alloy
  ~ 8 wt% P
  NiP + Ni_2P eutectic/amorphous
  80 μm thick film deposit on Cu substrate
  30% of reflection coeff.

* etching process by sulfuric/nitric acids
  10 μm of etching depth
  porous/rough surface (velvet)
  nickel phosphate compounds
  Ni + (H_2) PO_4 + (H_2O)
  0.2% of reflection coeff.



outgassing rate measurement (throughput method)

* large amount of hydrogen gas inclusion



Black NiP

エラストマ等のガス放出速度