

**NACE Jubail  
Technical Meeting**

**05-01-2010**

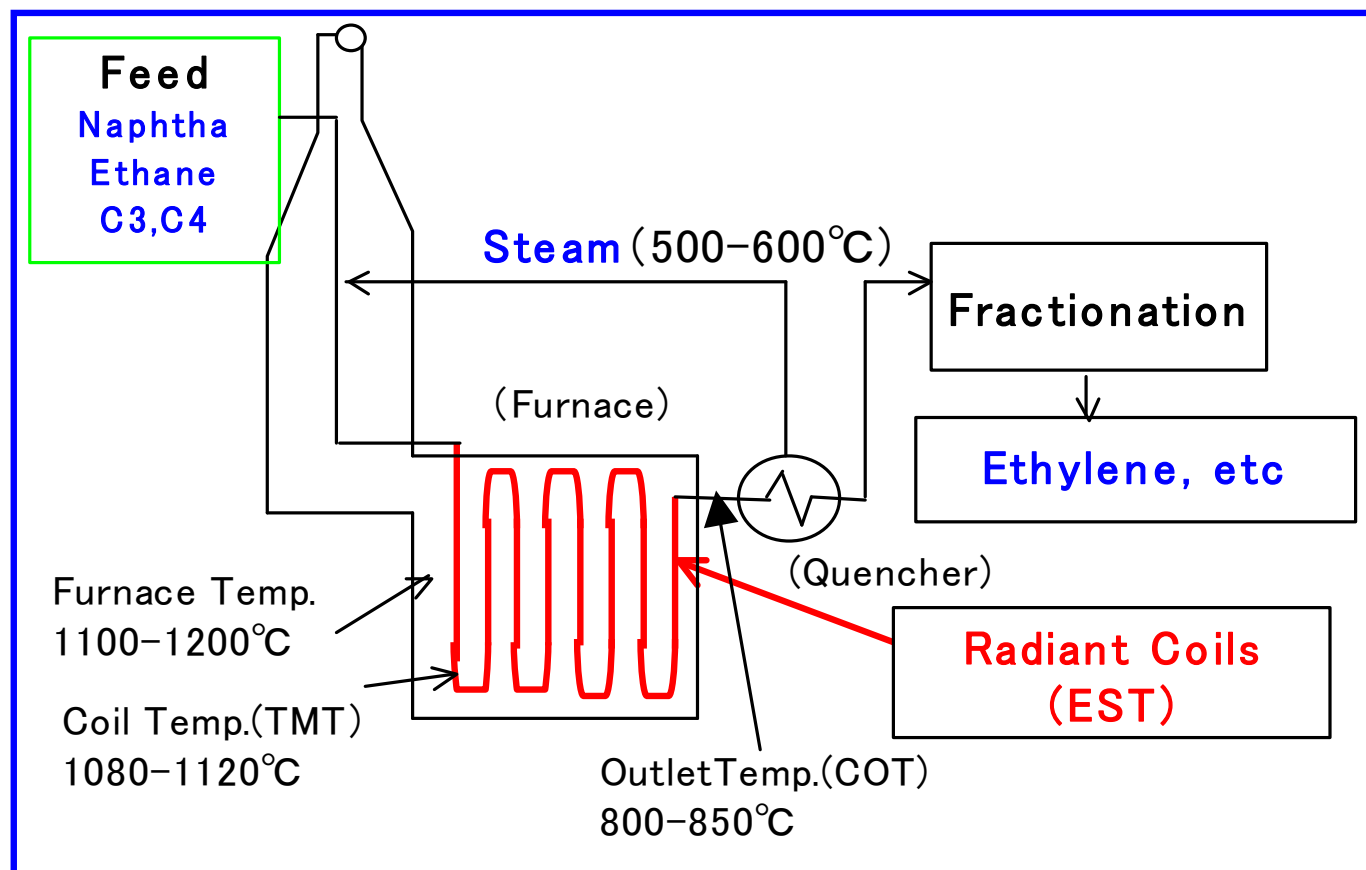
**Daido Steel Co., Ltd**

# Daido's New Materials for Petrochemical industry And Energy industry

1. **EST** (Ethylene Super Tube)
2. **BST** (Boiler Super Tube)
3. **DSA760** (Ni-38Cr-3.8Al )

# EST (Ethylene Super Tube)

## Ethylene Furnace



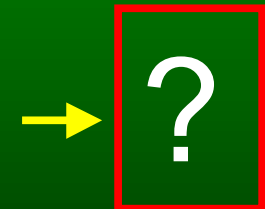
# Introduction

History of radiant coils for ethylene pyrolysis furnace material:

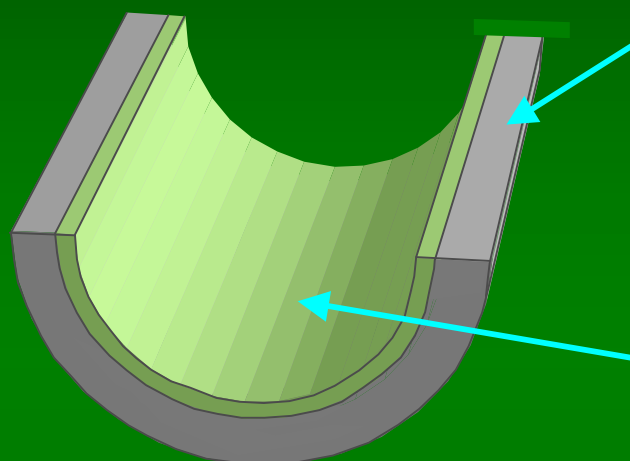
A constant struggle for longer life & run length at higher temperature & severity



			→ 2007
18Cr-8Ni (304) 25Cr-20 (310)	25Cr-20Ni (HK) INCO 800	25Cr-35Ni (HP)	25Cr-35Ni-Nb (HP-Nb) 35Cr-45Ni



Our Solution: **EST** (Ethylene Super Tube)  
= PPW (Plasma Powder Weld) Overlaid Tube



### Base Tube

- Material: Conventional (HK, **HP-Nb**, 35Cr-45Ni, etc.)  
Centrifugally cast (Daido)

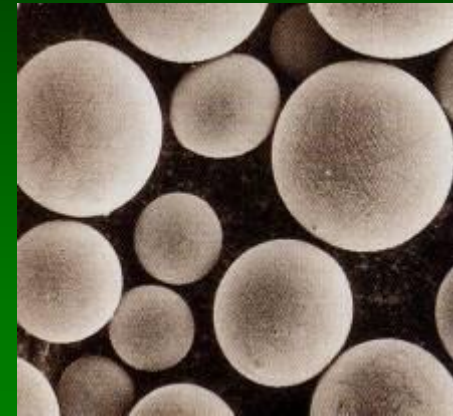
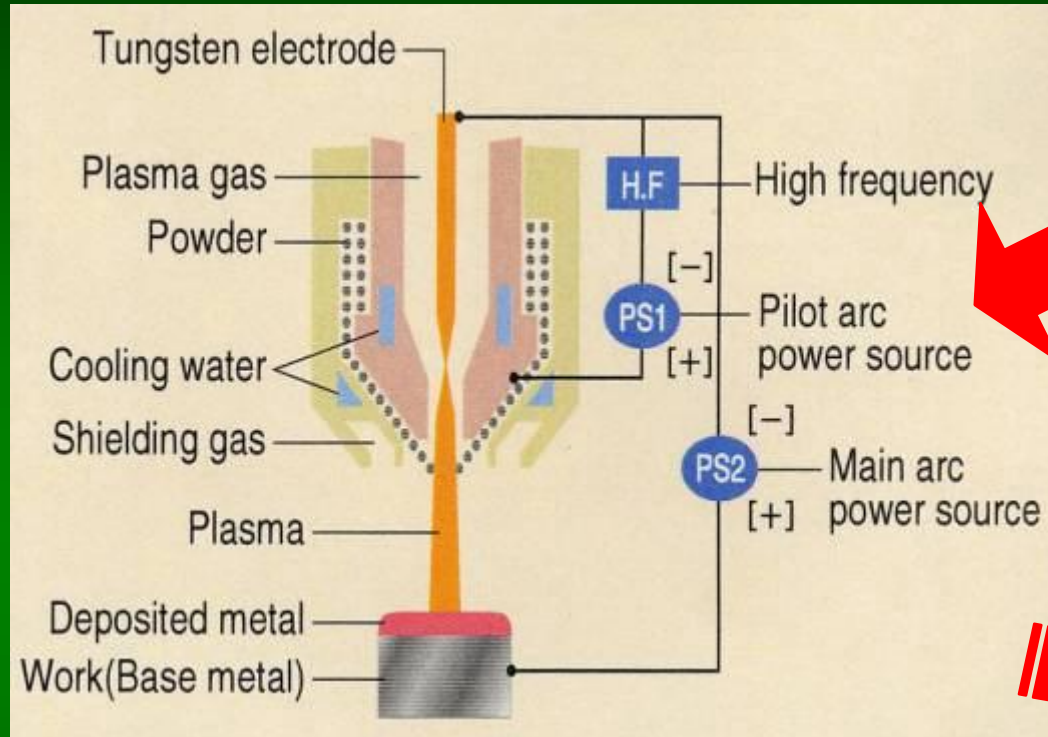
### PPW layer

- Material: **45Cr-50Ni-1Mo**  
Gas atomized & PPW'd (Daido)
- Thickness: 1 - 3 mm

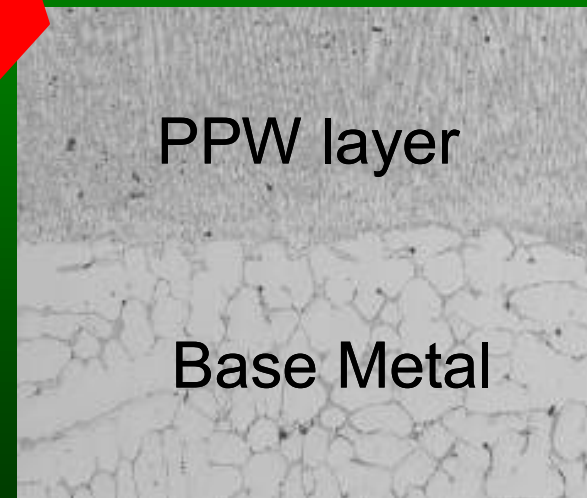
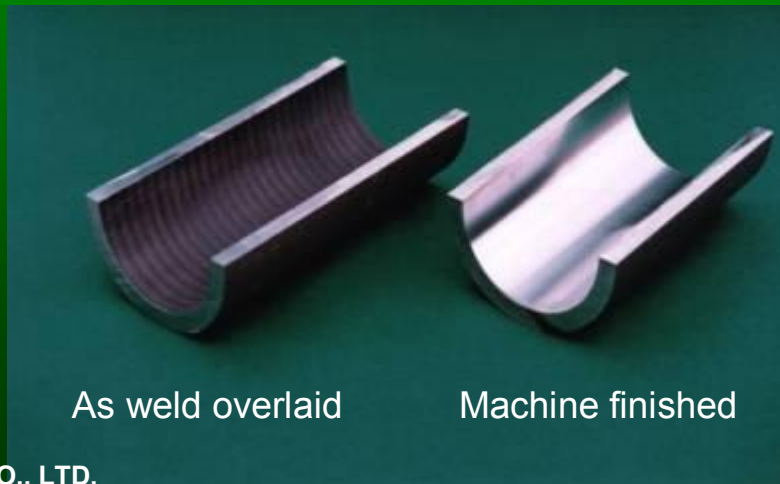
## Main Benefits

- Anti Catalytic Coke
- Anti Carburization

# PPW (Plasma Powder Welding)



Gas atomized 45Cr-50Ni-1Mo powder



PPW layer

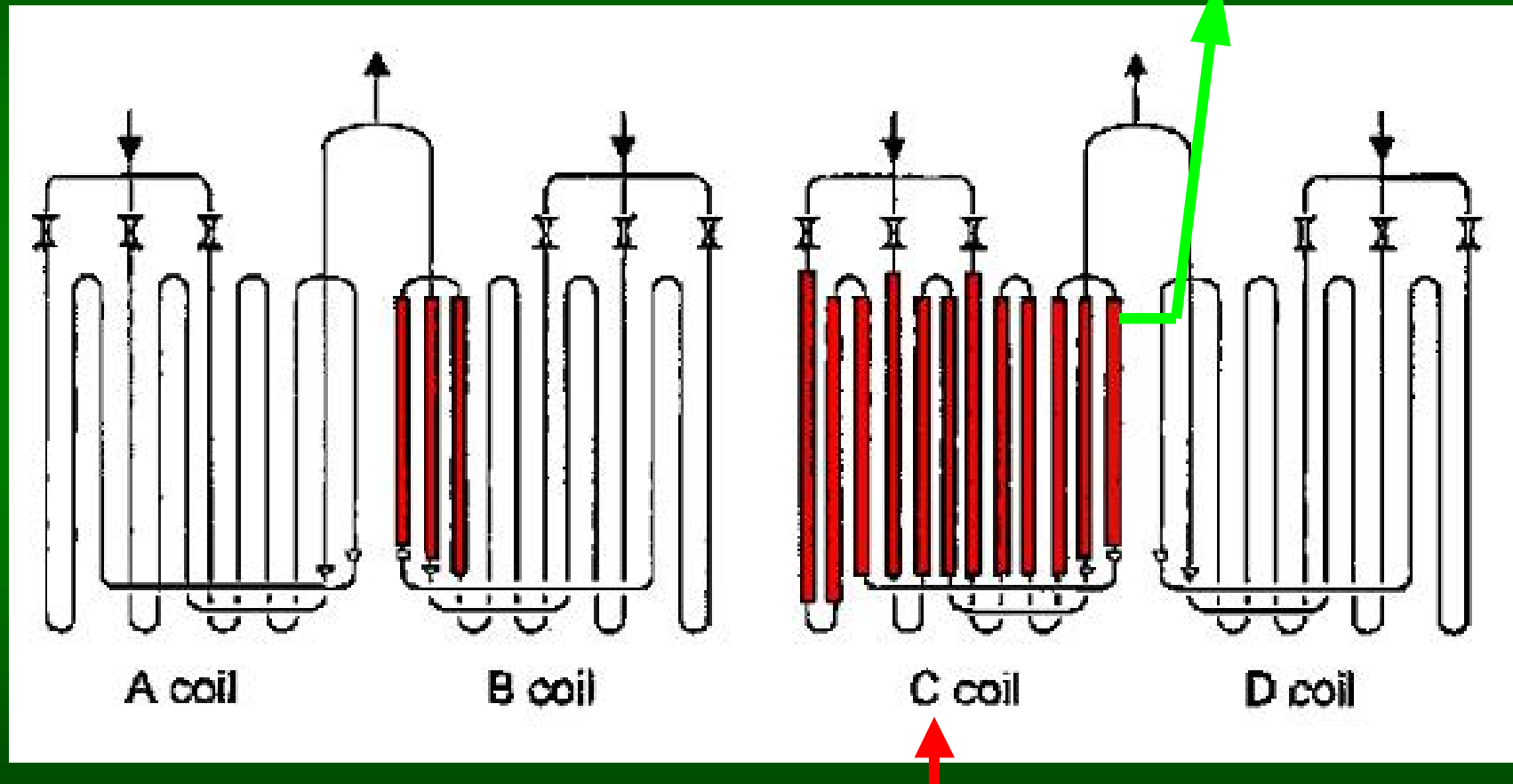
Base Metal

# Anti-Carburization

The PPW layer stops carburization into the base tube by the “Dam-Effect”.

# Furnace A: Naphtha Feed

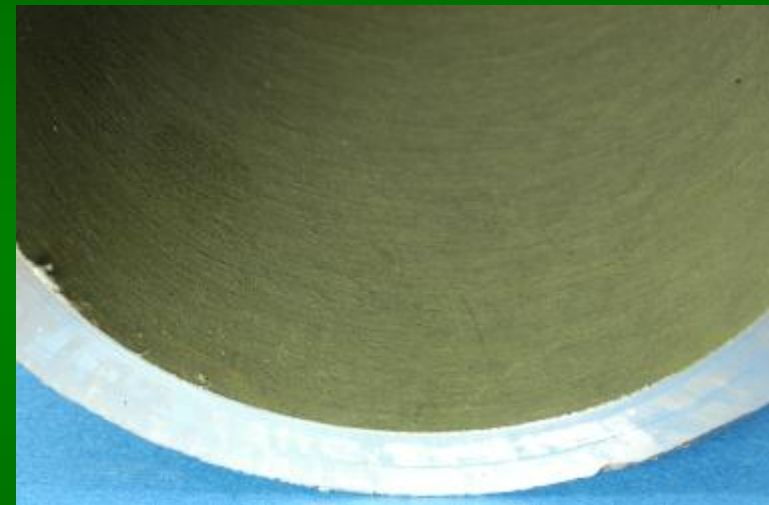
Samples taken after 9 years of operation



Coils with EST have been used since 2000.



# Appearance of EST (After 9 years)

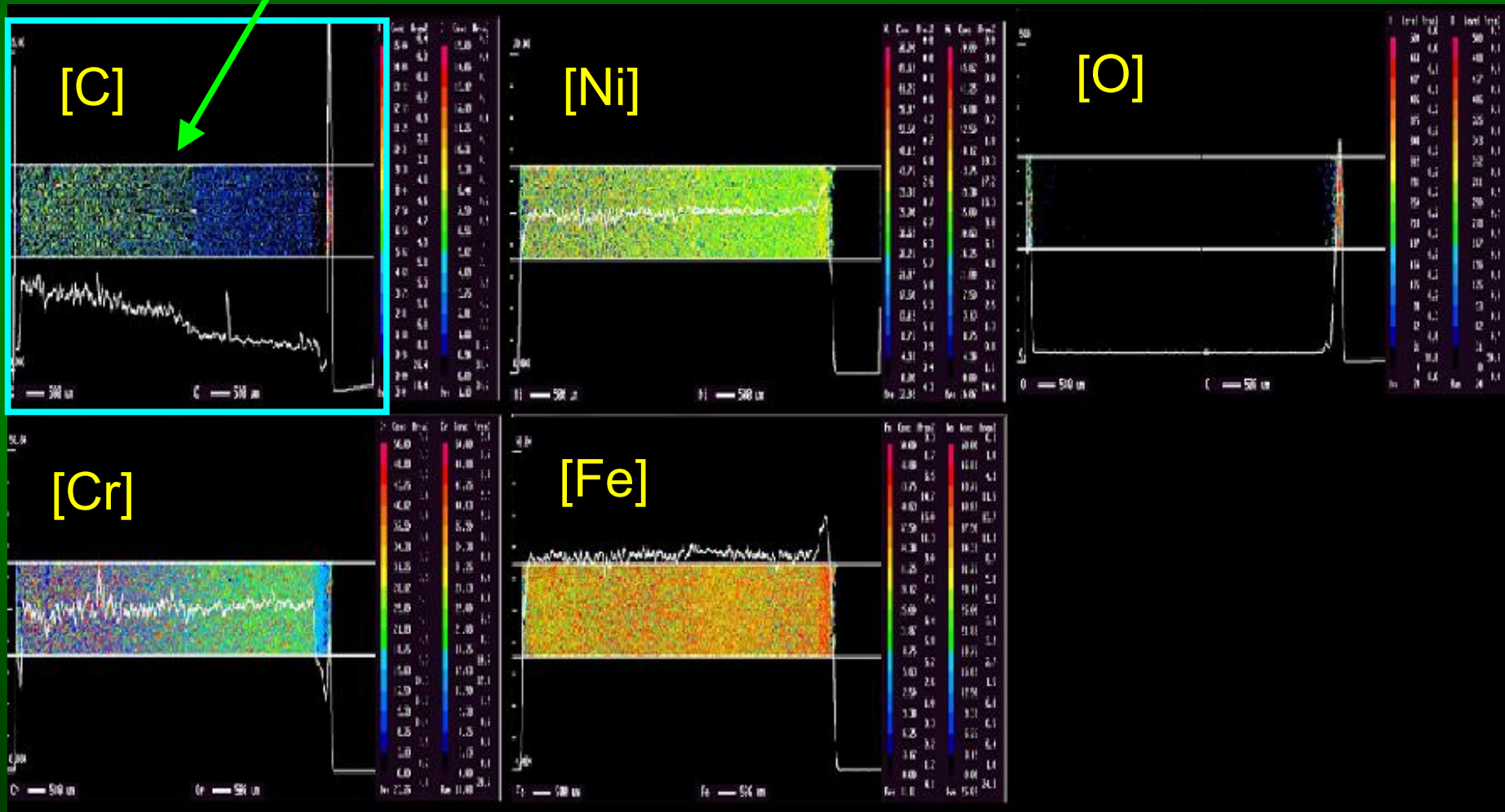
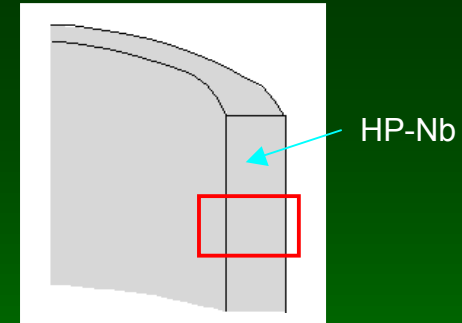


- Green colored surface is recognized. (same as the sample after 24 months)
- No-erosion or damage is observed.

# Cross Section Composition Analysis

HP-Nb, after 2 years of operation

- Fully carburized.
- [C]: 4.7% (ID), 1.1% (OD)

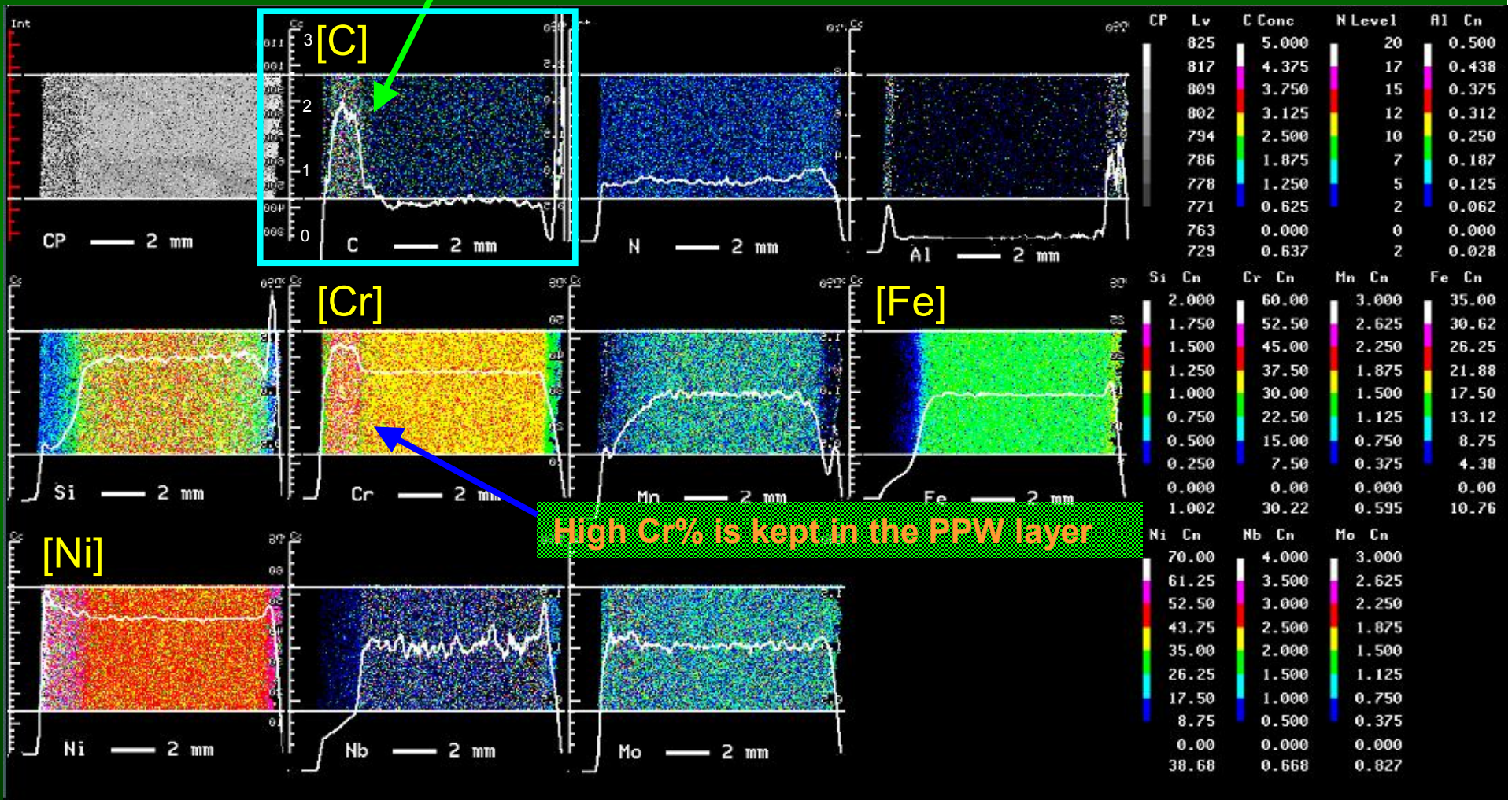
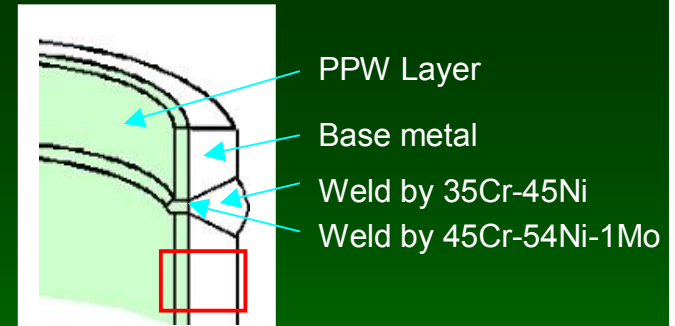




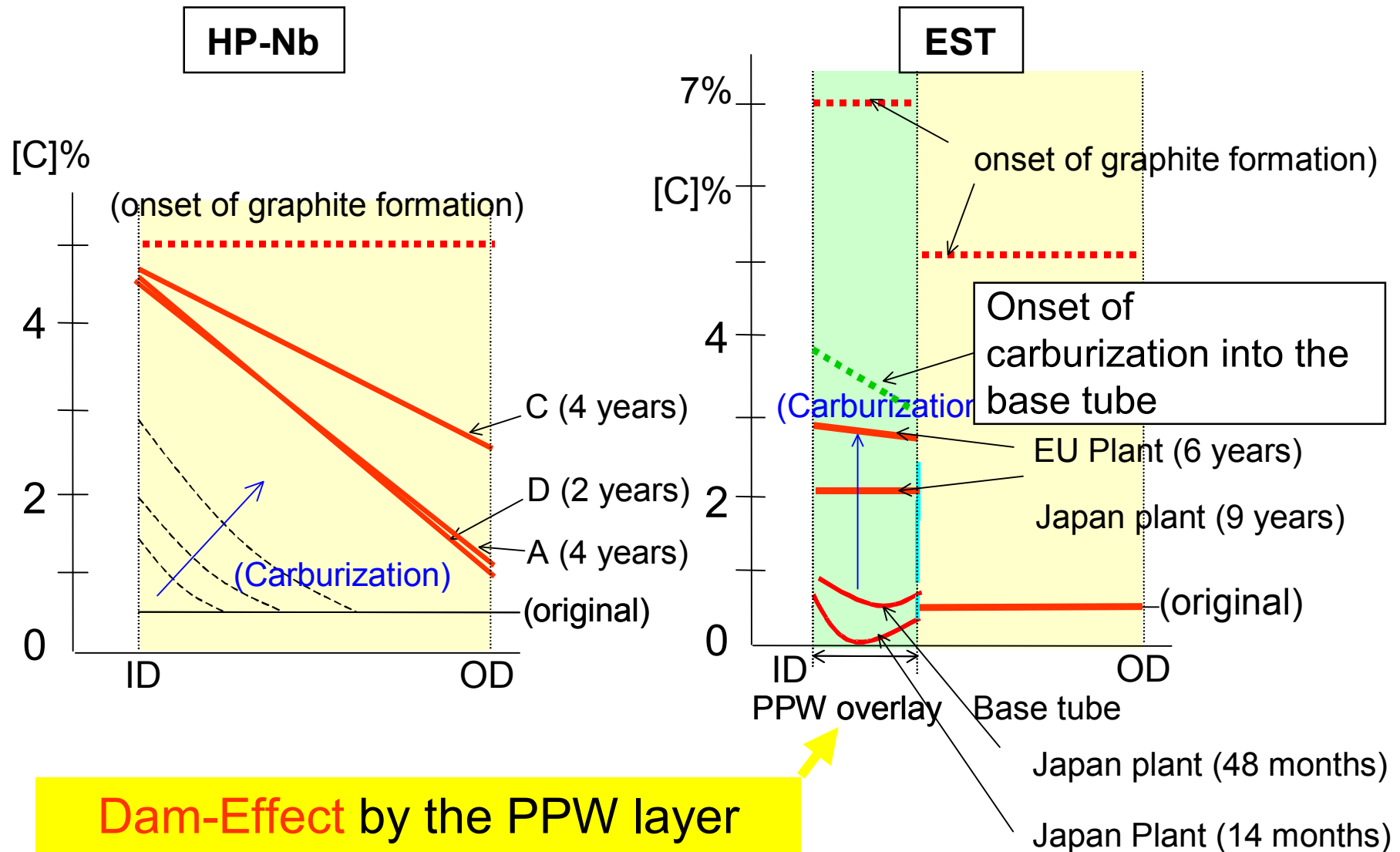
# Cross section composition analysis

**EST**, after 6 years of operation

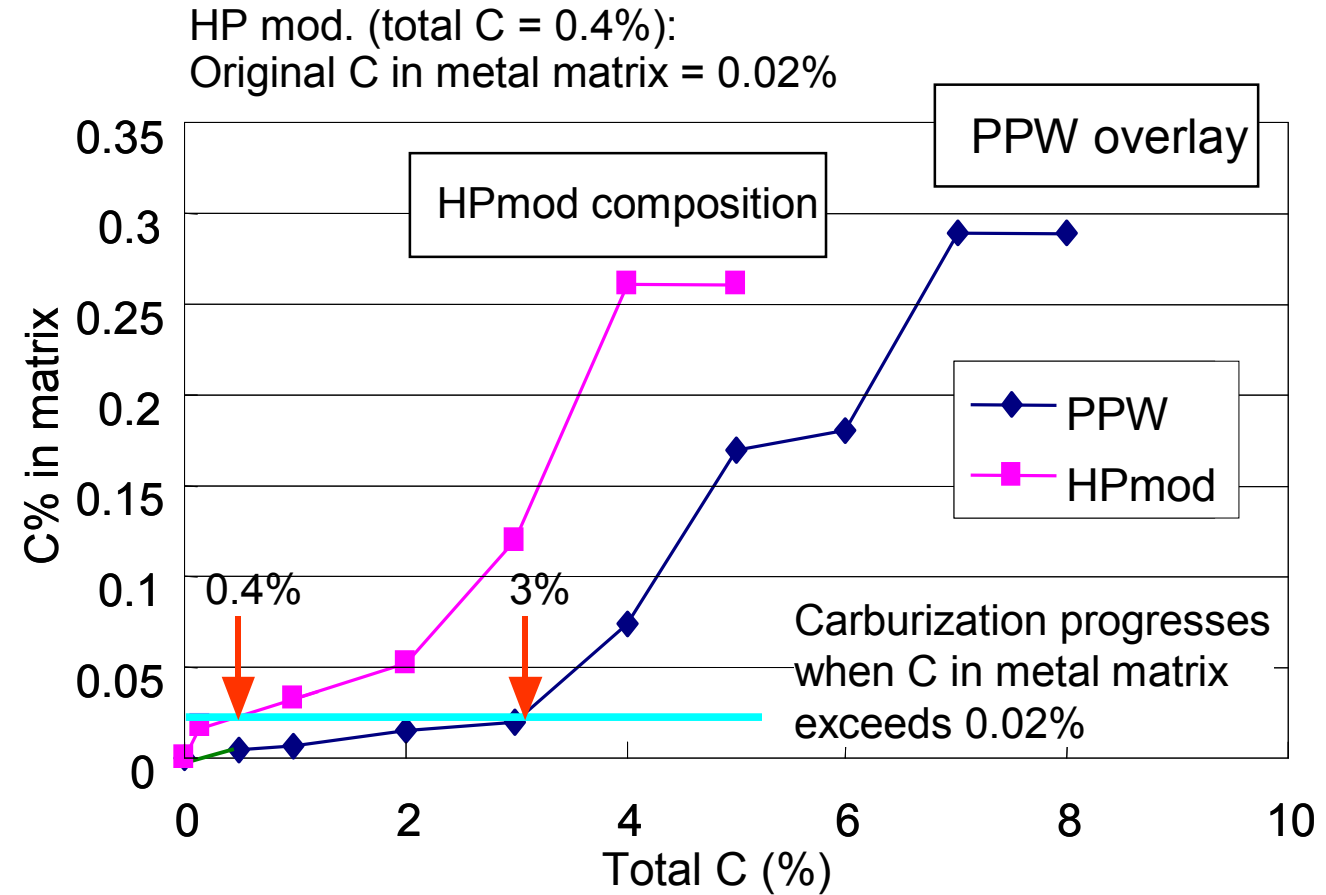
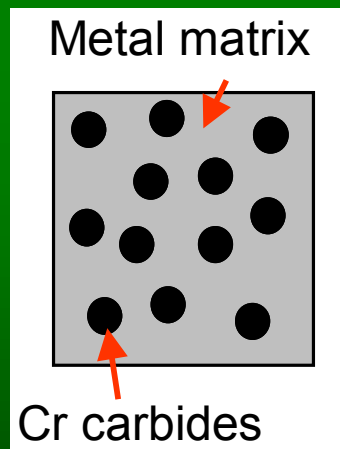
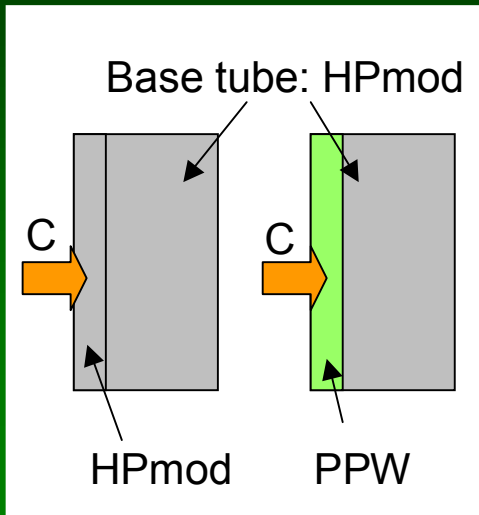
- Carburization stops at the PPW layer
- No-carburization in the base tube



# Actual Carburation Comparison



# Mechanism of Dam-effect



“Dam-effect” can only be expected in the clad tubes, not in solid tubes.

Lack of carburization in EST can prevent physical distortion and help maintain stable operation.



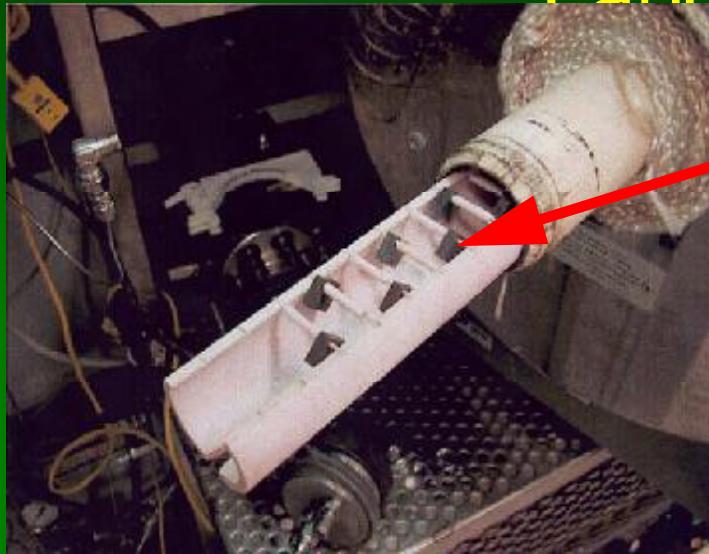
# Anti Catalytic Coke

An Fe free, Cr-oxide film  
on the PPW layer  
reduces catalytic coke formation  
with “Self Healing Effect”.



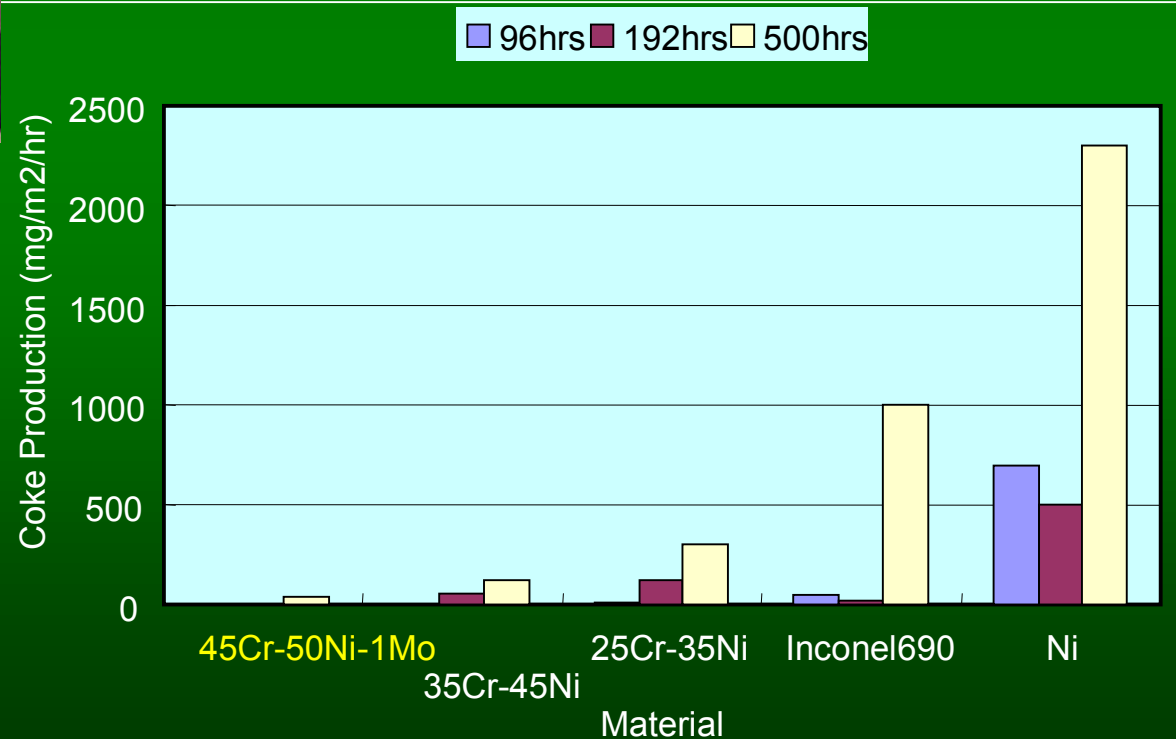
# Coke Resistance

## Laboratory screening



Metal coupons in hot gas stream accumulate coke as experiment proceeds. Coupon EST is prepared by PPW process

Simulated process gas environment

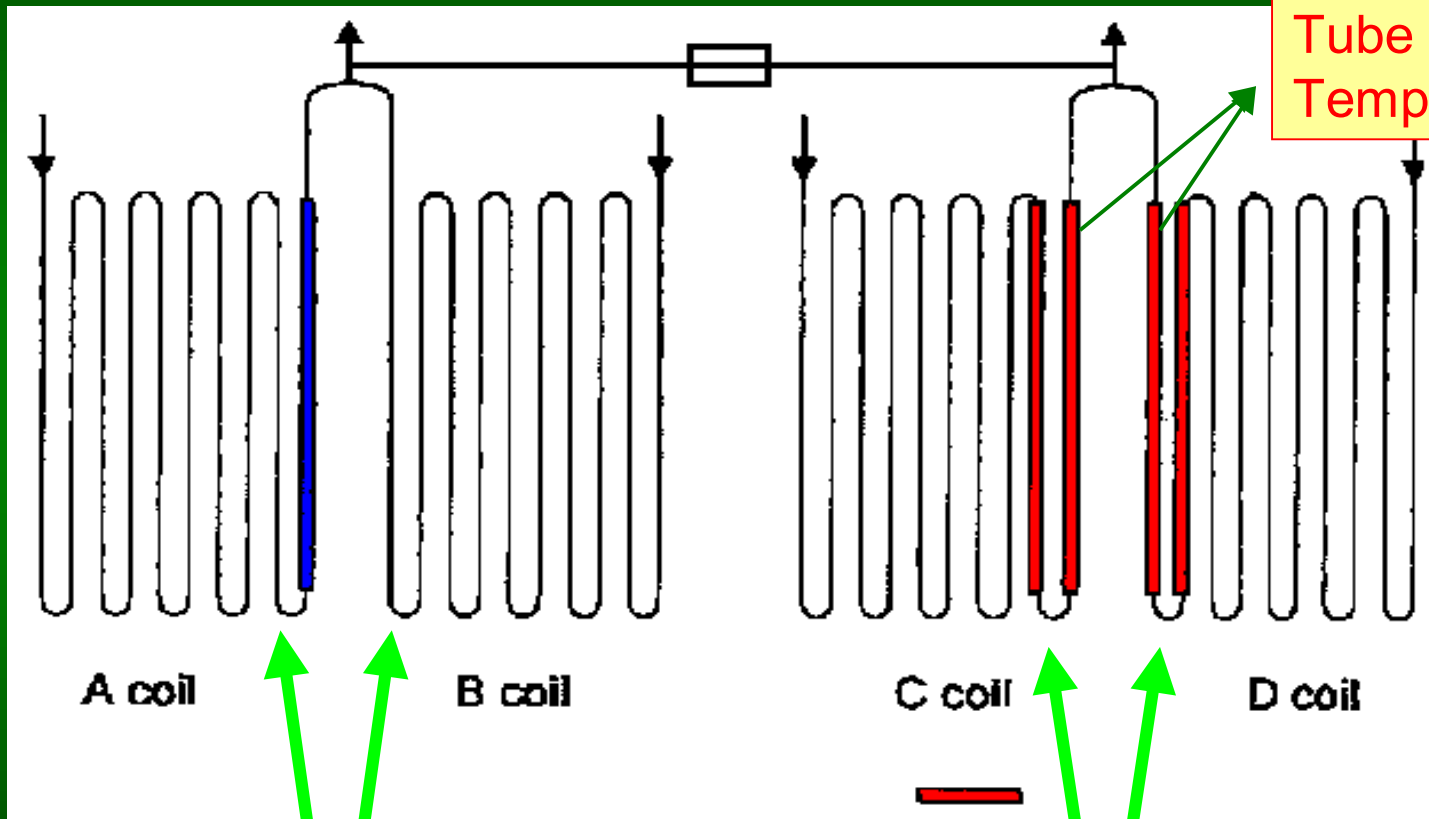




# Furnace B: Gas Feed

TLE No.2

TLE No.1



Tube Metal Temperature

A coil

B coil

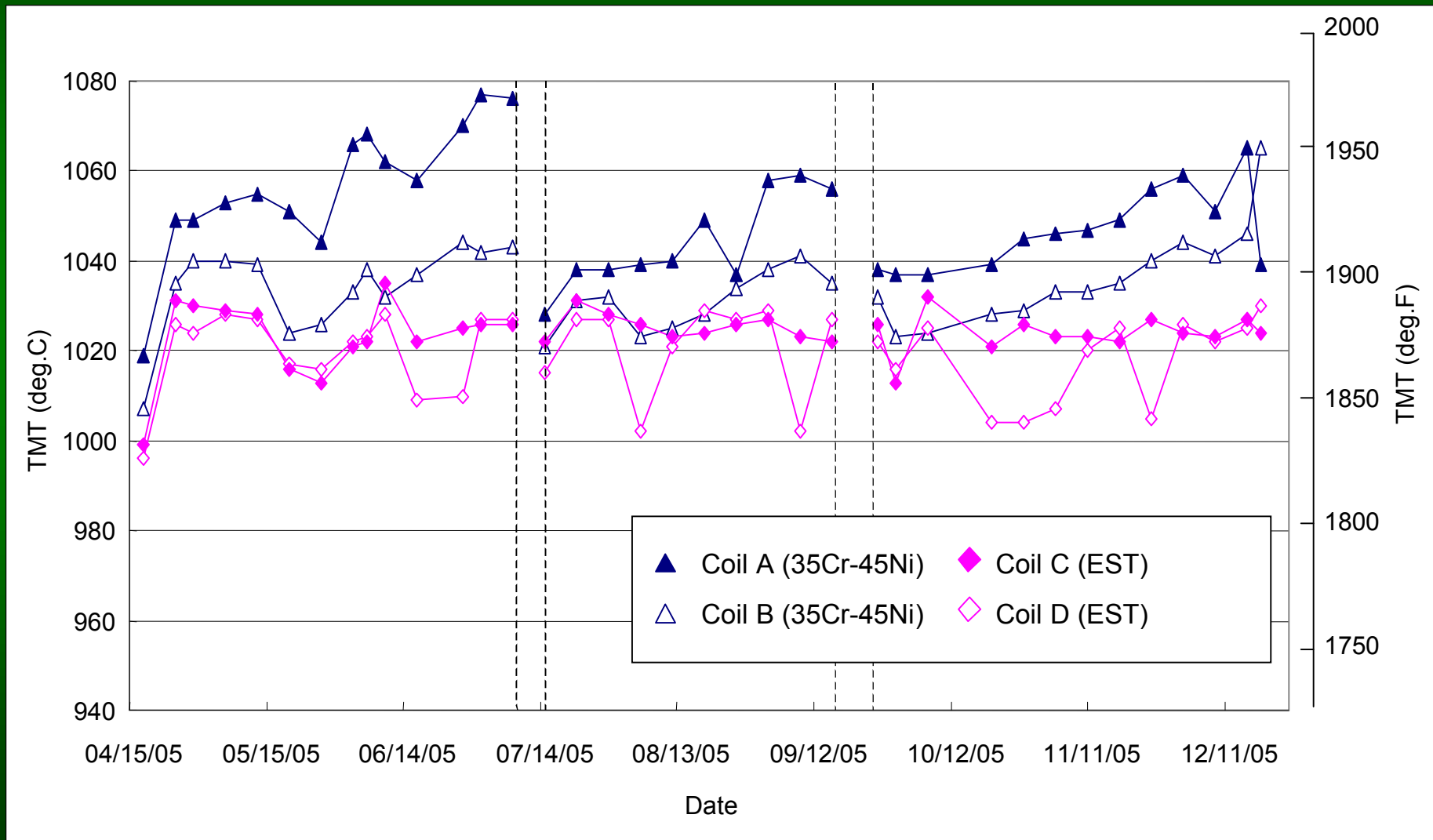
C coil

D coil

35Cr-45Ni

Coils with EST  
(2 out of 10 passes )

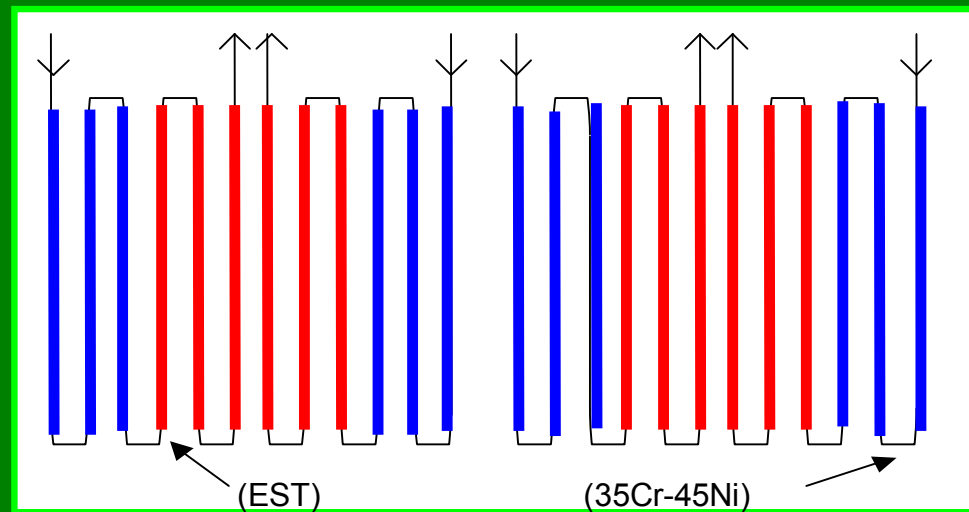
# Furnace B: TMT (Flat means less coke formation)



# Furnace C/D: Gas Feed

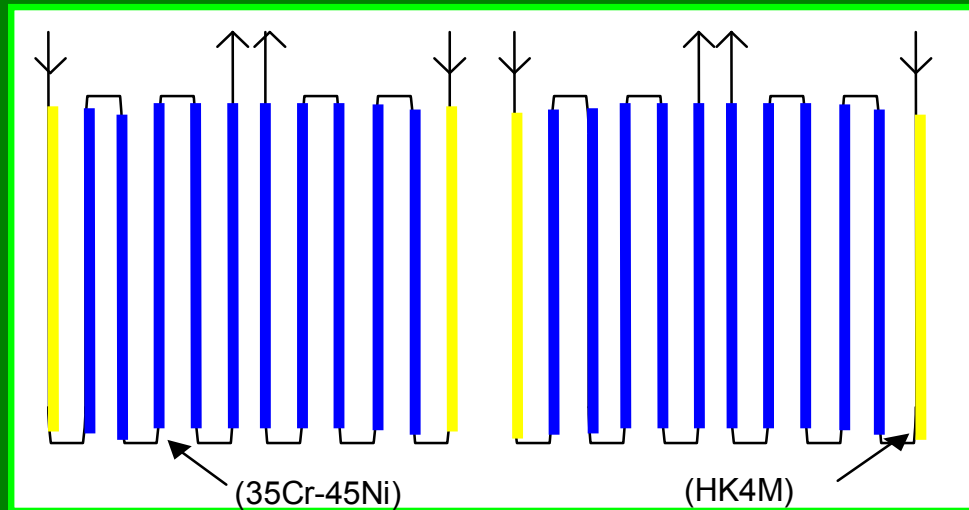
Furnace C:

**EST** used for 50%  
of full coil

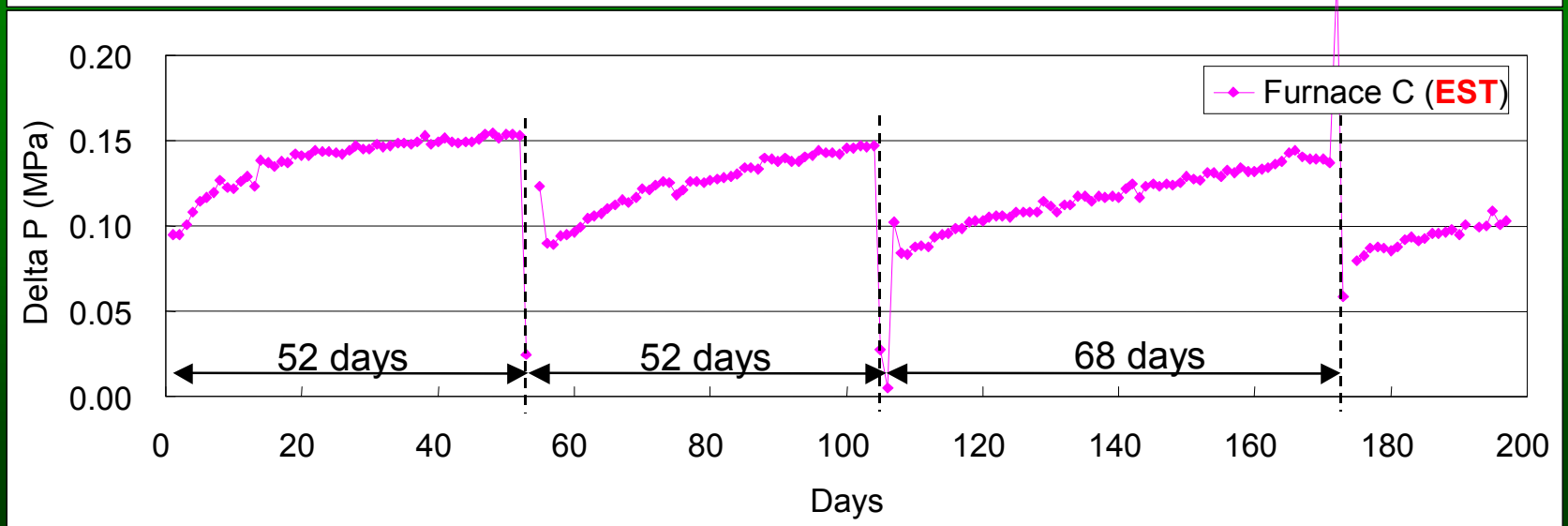
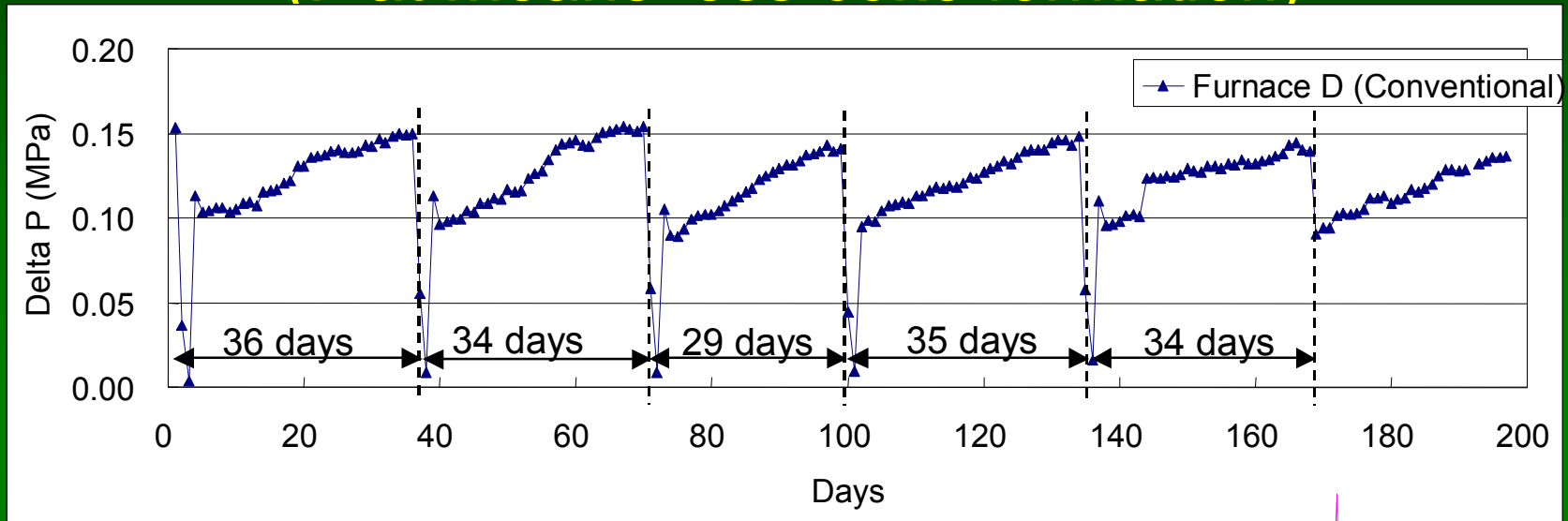


Furnace D:

Identical furnace  
with **35Cr-45Ni**

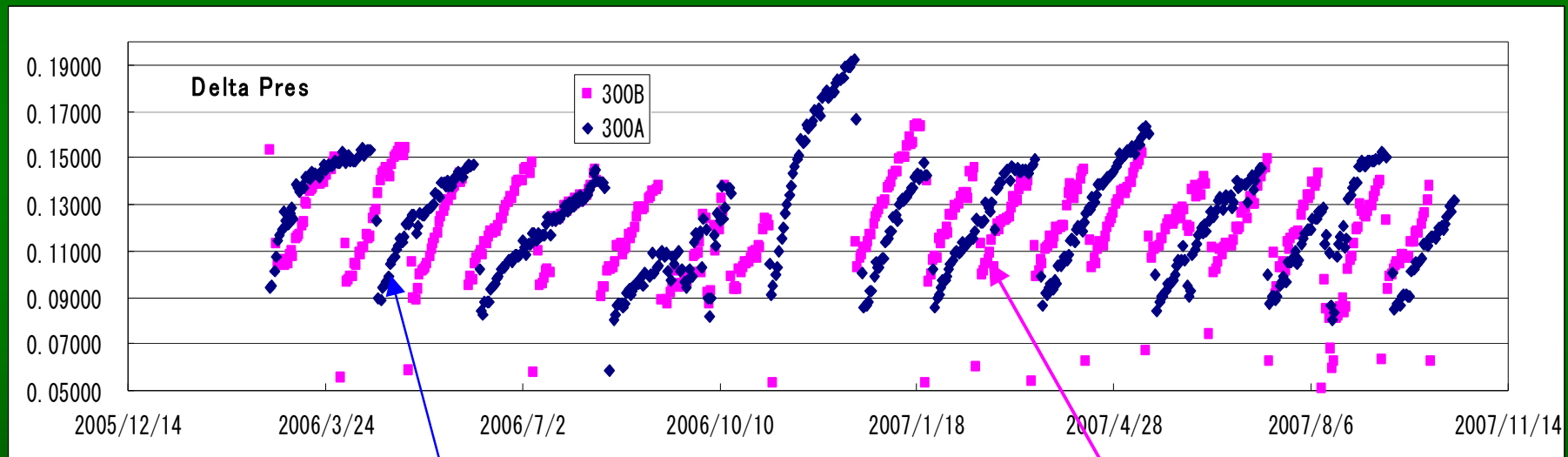


# Furnace C/D: Pressure Drop (Flat means less coke formation)



# Lower pressure increase continue through years by “Self Healing Effect” of EST

2 years

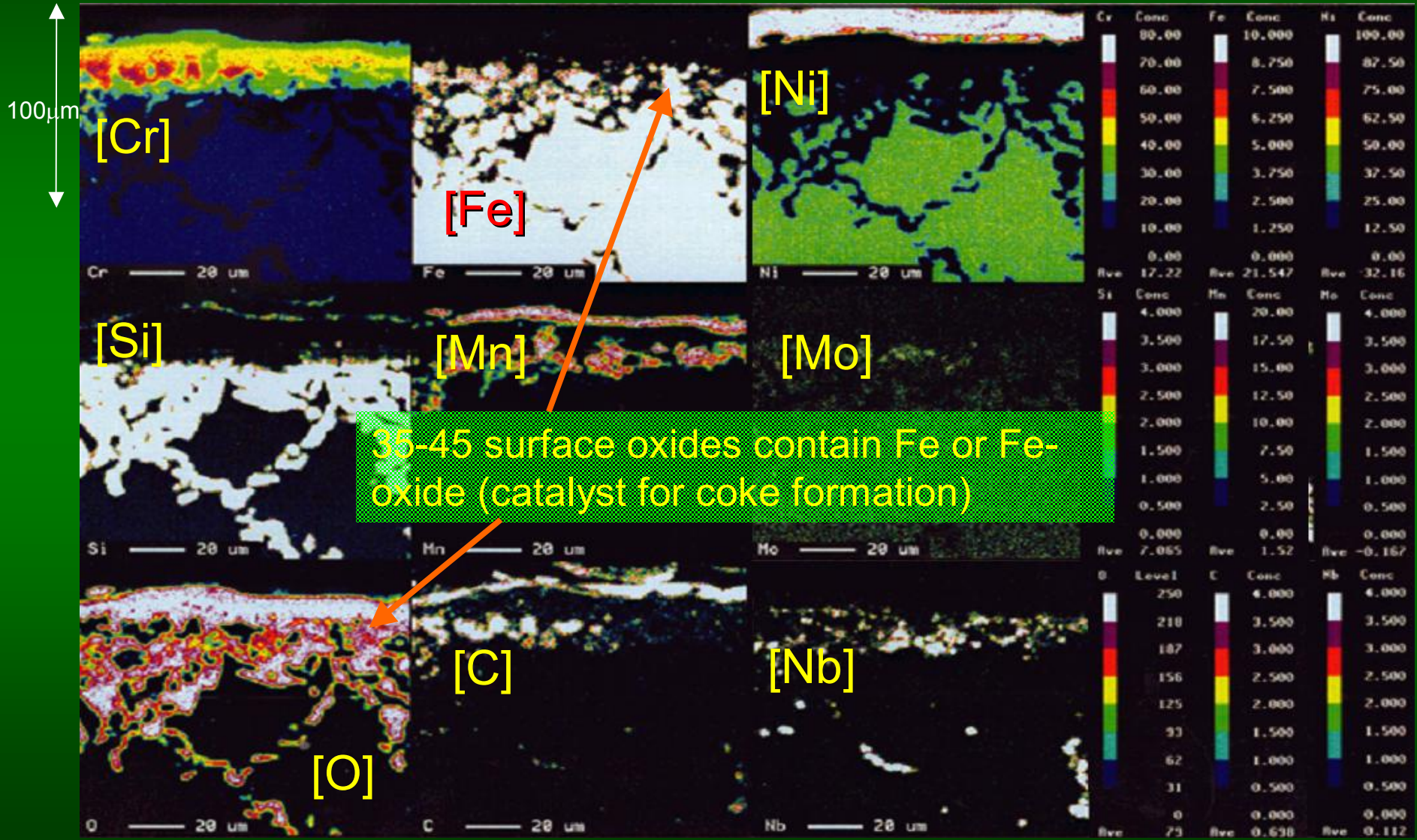


FurnaceC : EST

FurnaceD : 35Cr – 45Ni

# Surface composition mapping of 35Cr/45Ni after 3.3 years

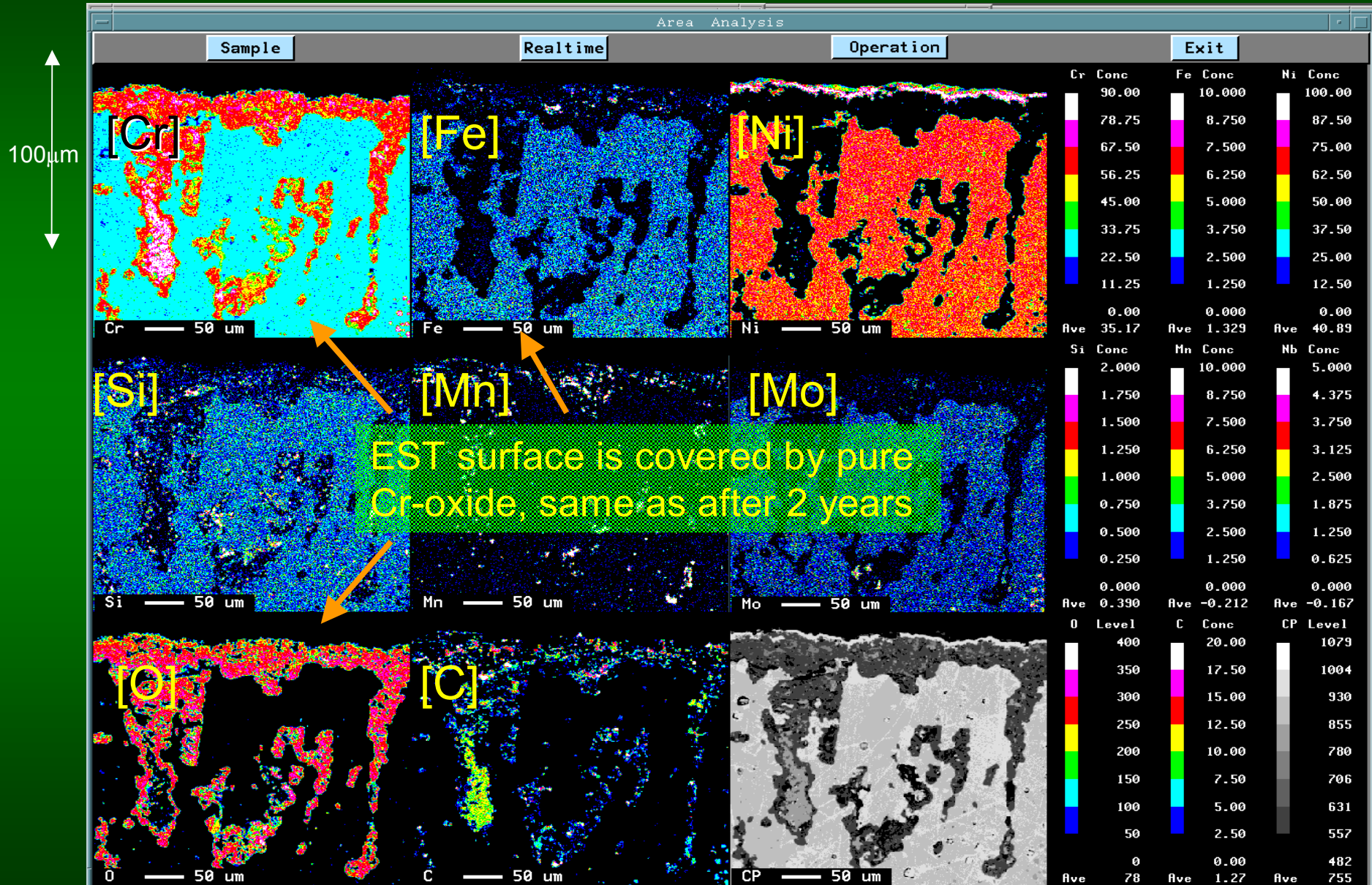
Near ID surface



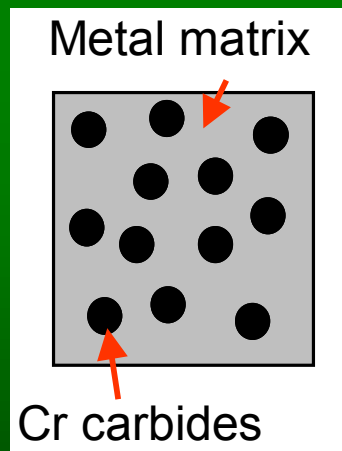
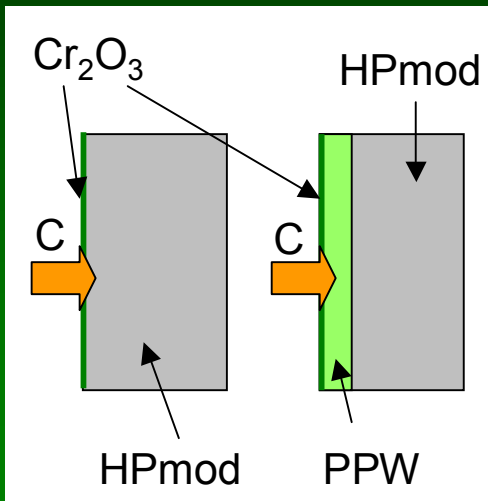


# Surface composition mapping of EST after 9 years

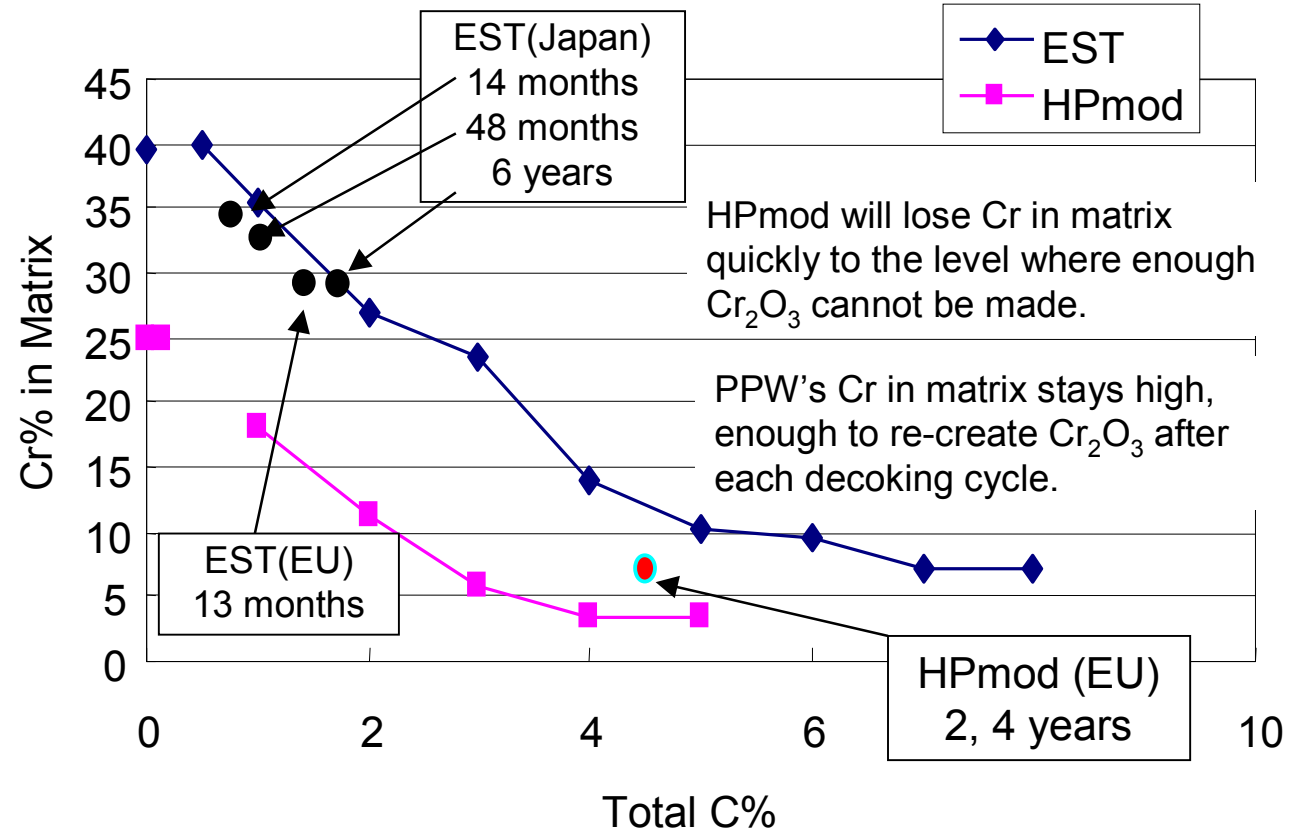
Near ID surface



# Mechanism of Self-healing



As the alloy is carburized, Cr in metal matrix will be depleted (forming Cr-carbides) and lose the ability to form surface Cr<sub>2</sub>O<sub>3</sub>.



Due to high Cr in the PPW layer, surface Cr<sub>2</sub>O<sub>3</sub> can be re-created and reinforced after each decoking cycle: **“Self-healing effect”**



# Summary

EST has,

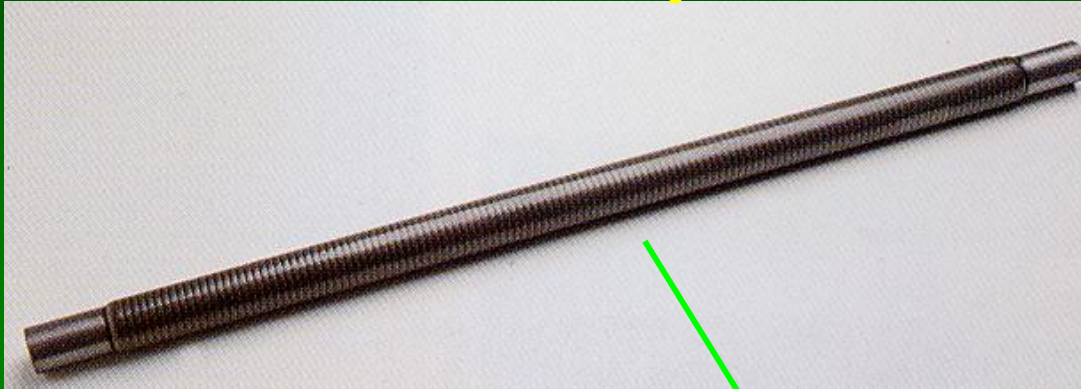
- Extremely high carburization resistance
  - à Extended tube life (Twice or more)
  - à Ability to run at higher severity
  - à Maintained ductility (can survive emergency shutdowns)
- Suppression of catalytic coke formation
  - à Extended run length (Twice in ethane furnace)

Higher pricing than conventional tubes, but Pay back In a year can be expected.

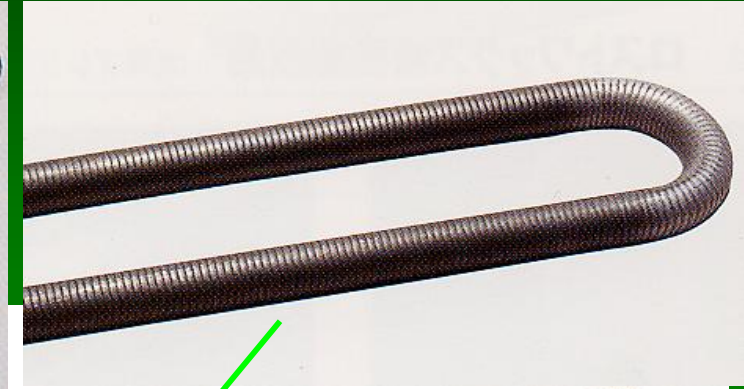
(EST is in operation at over 10 commercial plants)

# BST (Boiler Super Tube)

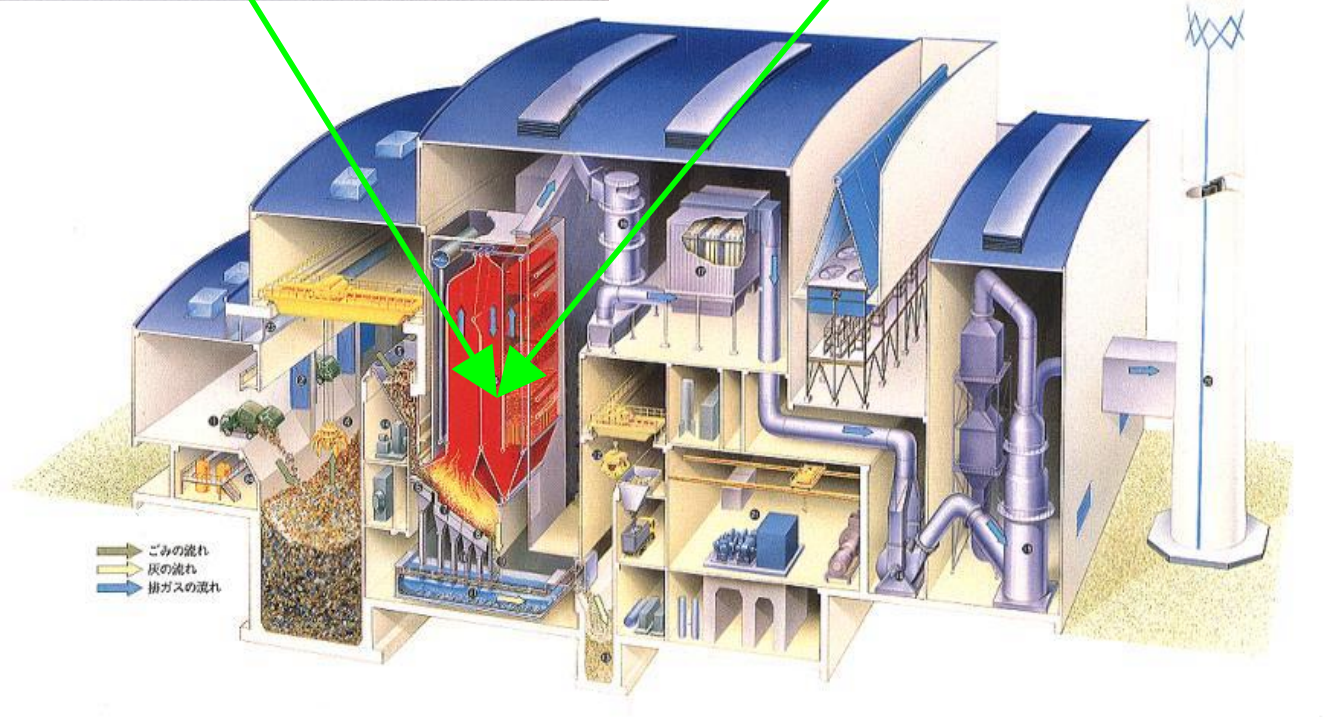
Outer surface overlay



Overlay and bending

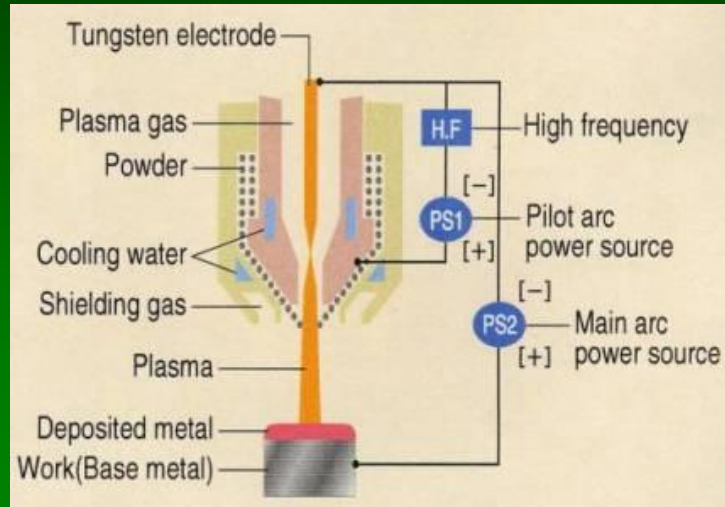


Waste to  
Energy plant

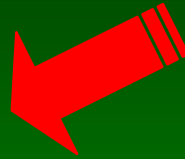
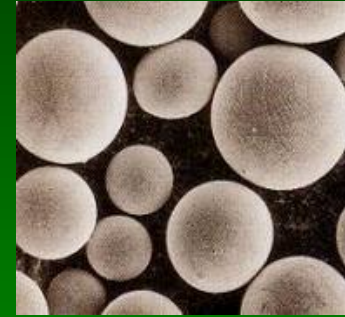


# Benefits of **BST** (Boiler Super Tube)

## Plasma Powder Welding



## Original metal powder



## BST Production Line



## "Boiler Super Tube"



**Anti-corrosion to corrosive fired gas in high temperature**



**Higher steam temperature for Higher efficiency of power generation**

# History of **BST** (Boiler Super Tube)

- 1960-1964 Union Carbide Co. in USA developed welding application of plasma energy and powder metallurgy.
- 1973-1991 Daido Steel developed automatic **Plasma Powder Welding (PPW) equipment for engine valves**.  
Plasma arc generator, gas controller, powder metal feeder, and particle size control were patented by Daido.
- 1992- More than 150 PPW equipment for engine valves have been shipped to automotive engine valve manufacturers.
- 1994- Daido developed **Boiler tubes with PPW overlay for the waste to energy plant through a Japanese National Project**.
- 1998- Daido started commercial manufacturing of boiler tubes with PPW overlay as **1<sup>st</sup> Generation Boiler Super Tube "BST276, BST625"** for Japanese waste to energy plants.  
Daido developed new process for **PPW overlay on the inner surface**.
- 2009- Daido developed **New "BST1"** for higher temperature operation.

# 1<sup>st</sup> generation "BST 276 and BST 625"

(Steam Temperature: ~400°C)

Chemistry of Weld overlay (typical)

(wt%)

	C	Si	Mn	Ni	Cr	Mo	Co	W	Fe
BST276	0.01	0.8	0.2	Bal.	20.8	13.2	2.2	3.1	1.0
BST625	0.01	0.2	0.1	Bal.	21.8	9.2	2.0	-	1.2

**Actual corrosion depth in the waste to energy plant** (550°C x 6000 hrs)



(Ref.) Mechanical Properties of Boiler tubes

STB340 + H-276M(PPW)		
R.T.		
	T/S	EI
Base tube	620	28.8
With PPW	601	41.2

(Base 5m/m + PPW 2m/m)



## Applications of “BST625 and BST276“ in Japan

Base tube	Size	OD: $\phi$ 38.1 - 114.3 mm, Thickness: 3.5 - 6.0 mm, L (shipping length): 0.9 - 7.4 m
	Grade	STB340, STB410, SUS310J1
PPW overlay	Thickness	2 - 2.5 mm
	Grade	276 modified, Inco625, 625modified
Installation	24 Waste to Energy Plants in Japan (Locations: Tokyo, Osaka, Nagoya, Hokkaido, Tochigi, Kyoto, Kagawa, Toyama, Chiba, etc)	
Remarks	Over 8000 pcs are in operation now. Maximum years in operation is 9 years. (2009)	

# New generation "BST1" for higher temperatures and longer tube life

(Steam Temperature: over 400°C)

## (1) Chemistry of PPW overlay

	C	Si	Ni	Cr	Mo	Co	W	Al
<b>BST1</b>	<b>Ad.</b>	<b>Ad.</b>	<b>Bal.</b>	<b>27</b>	-	-	<b>Ad.</b>	<b>Ad.</b>
BST625	0.01	0.8	Bal.	22	9	2	-	
BST276	0.01	0.2	Bal.	21	13	2	3	

## (2) Concept of **BST1**

- Chemistry of BST1 is originally developed and applied for **commercial Air-heater for Gasification and Ash Melting System.**  
(Metal temperature: 800°C (1,142°F))
- Higher corrosion resistance with **higher Cr** than BST625 or BST276.
- **Higher W** than BST276 prevents the formation of Cr-depleted zones.
- **Added Si, Al** prevent corrosion by Cl through grain boundaries.
- **Adequate C** makes fine grains to protect against corrosion through grain boundaries.

# Results of Corrosion Test

## JIS Z 2293

Methods for high temperature corrosion test of metallic materials  
by dipping and embedding in molten salts

### Salts

	Mol. %	Wt. %
Na <sub>2</sub> SO <sub>4</sub>	3	16.8
K <sub>2</sub> SO <sub>4</sub>	3	20.6
Fe <sub>2</sub> O <sub>3</sub>	2	12.6
PbCl <sub>2</sub>	3	28.15
FeCl <sub>2</sub>	3	12.85
NaCl	2	3.95
KCl	2	5.05

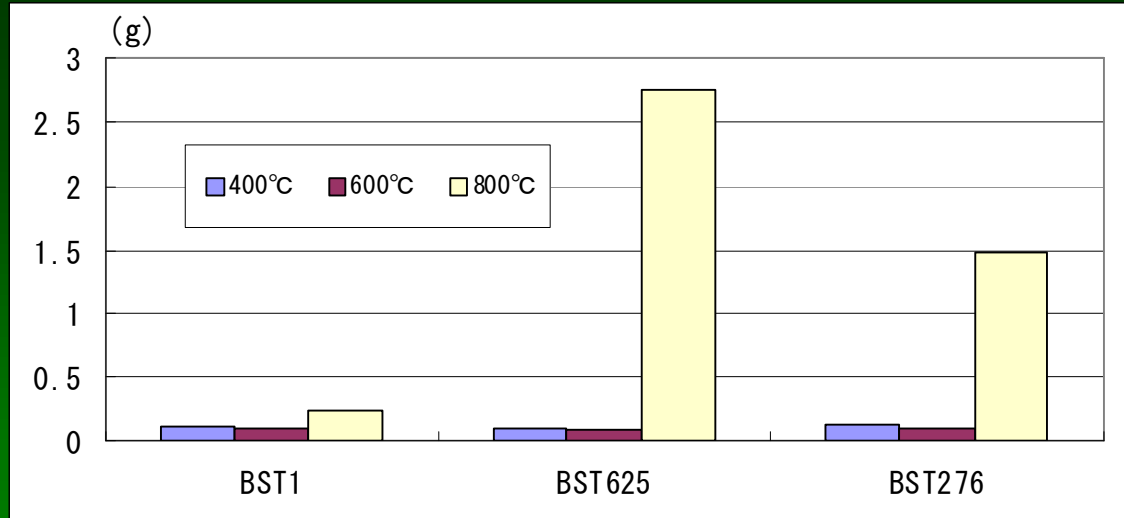
### Dipping temperature and time

°C	400	600	800
°F	752	1,112	1,472
time	100 hours		



# Weight loss

Weight loss of BST105 at 800°C is remarkably smaller than BST276 or 625



# Appearance after the test

	400°C x 100 h	600°C x 100 h	800°C x 100 h
BST1			
BST625			
BST276			

Almost no corrosion of BST1 even at 800°C

## Conclusions

- With higher contents of Cr, W, Al, and Si (with no Mo and Co), a new generation **BST1** has been developed.
- A high temperature (800°C or 1,472°F) molten salt test revealed **higher corrosion resistance of BST1** as compared with BST276 or BST625 against oxide and chloride formations.
- BST1 is expected to enable higher steam temperatures with longer tube life, resulting in **higher efficiency for waste to energy plant operation.**

# DSA760 ( Ni-38Cr-3.8Al)

## Characteristics

- **High hardness** in AG condition by precipitation of  $\alpha$ Cr and  $\gamma'$  phases
- **Wear resistance** comparing with AISI 440C
- **Corrosion resistance** in comparable with AISI 316
- **Easy to machine and cold work** in ST condition
- **Non-magnetic**

# Development History of DSA760

1972 (Japan)

Ni-40Cr-4Al (mass%) was developed by Toshiba for gas turbine parts, which had high hardness and good corrosion resistance.

1974 (Russia)

Ni-40Cr-3.8Al was introduced as high hardness and non-magnetic permeability alloy in a Russian paper.

1990 (UK)

Ni-40Cr-3.8Al was introduced again as the Russian Ni alloy and applied to a non-magnetic pressure cylinder.

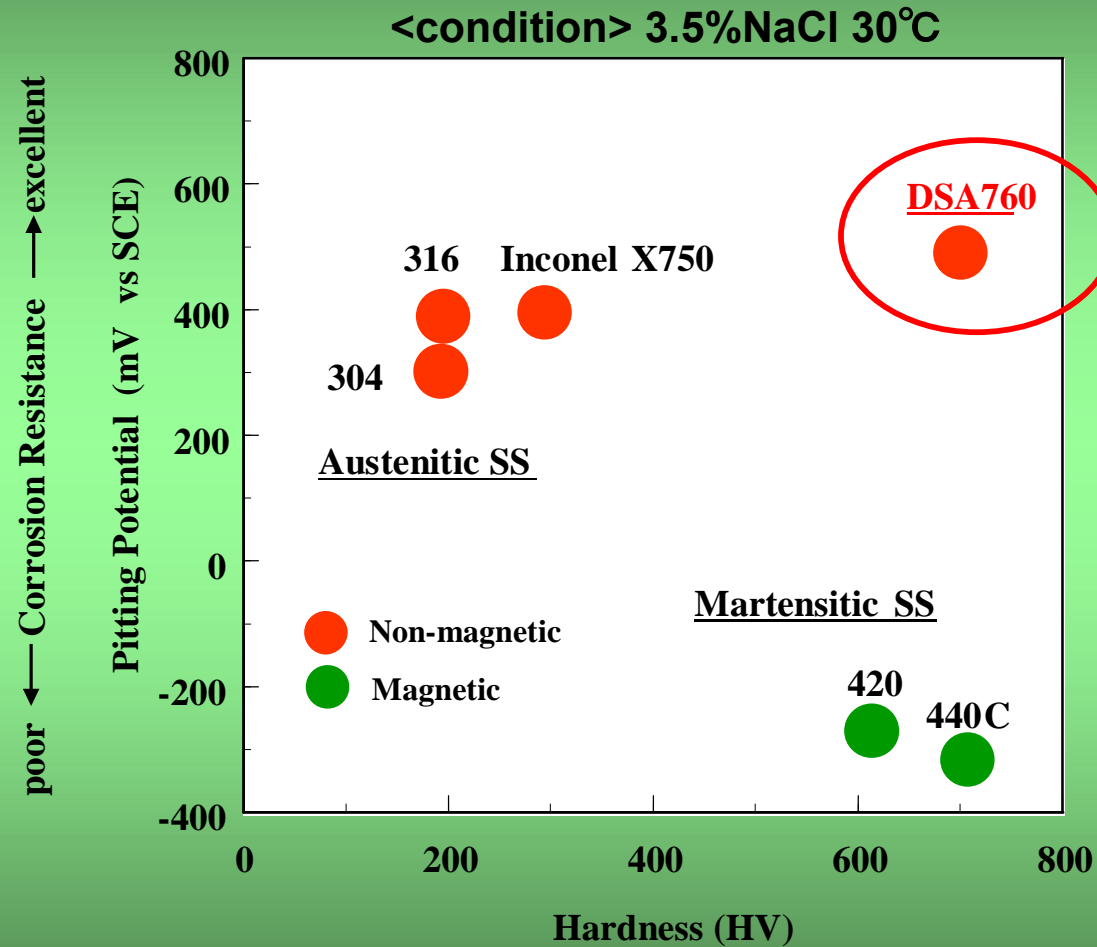
Manufacturing process was **cast** due to low hot workability.



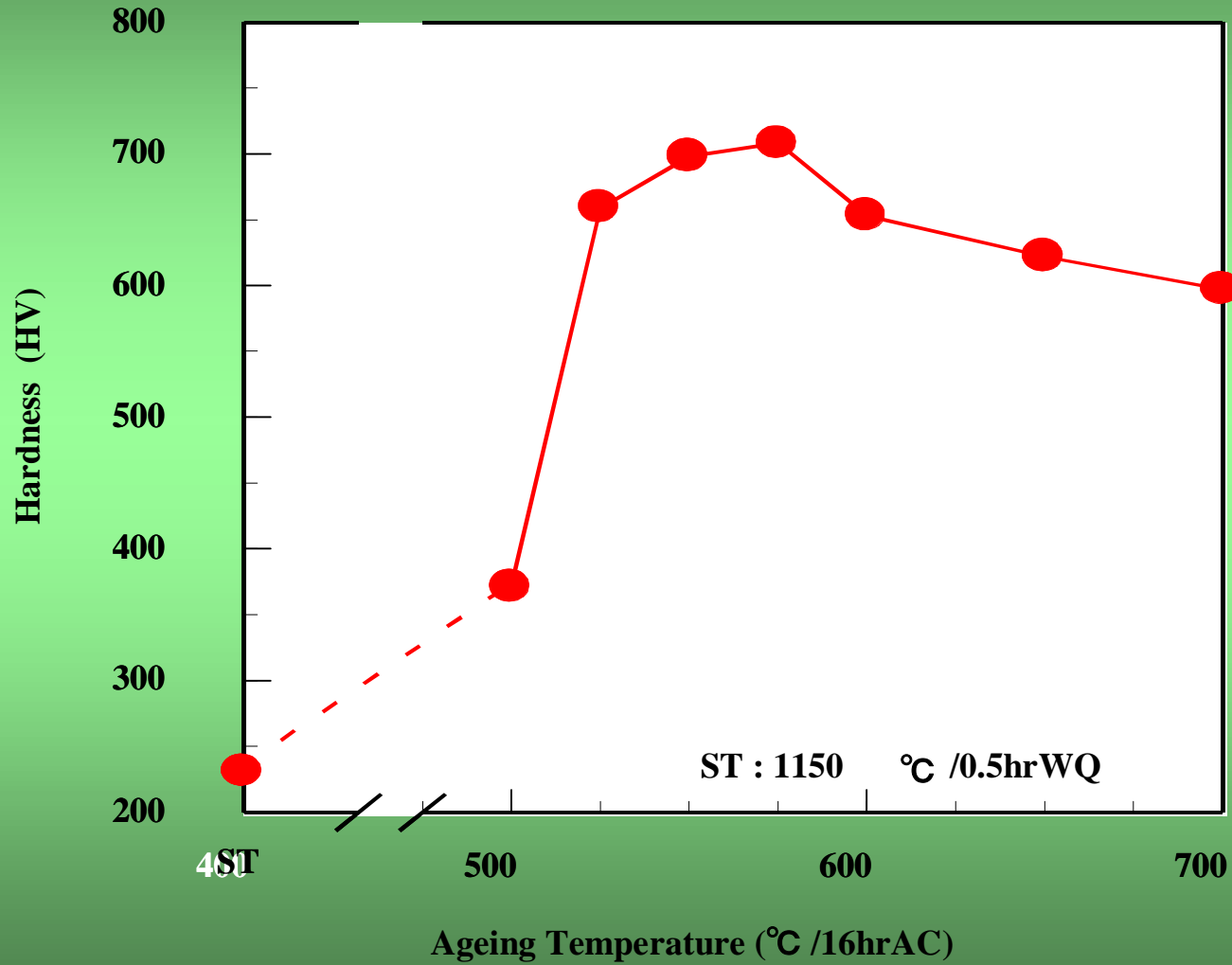
1999 - (DAIDO)

**DSA760** was developed for **forging and rolling** process to product many kind of products for every industry  
by **Daido process technology**

# Hardness and Corrosion Resistance

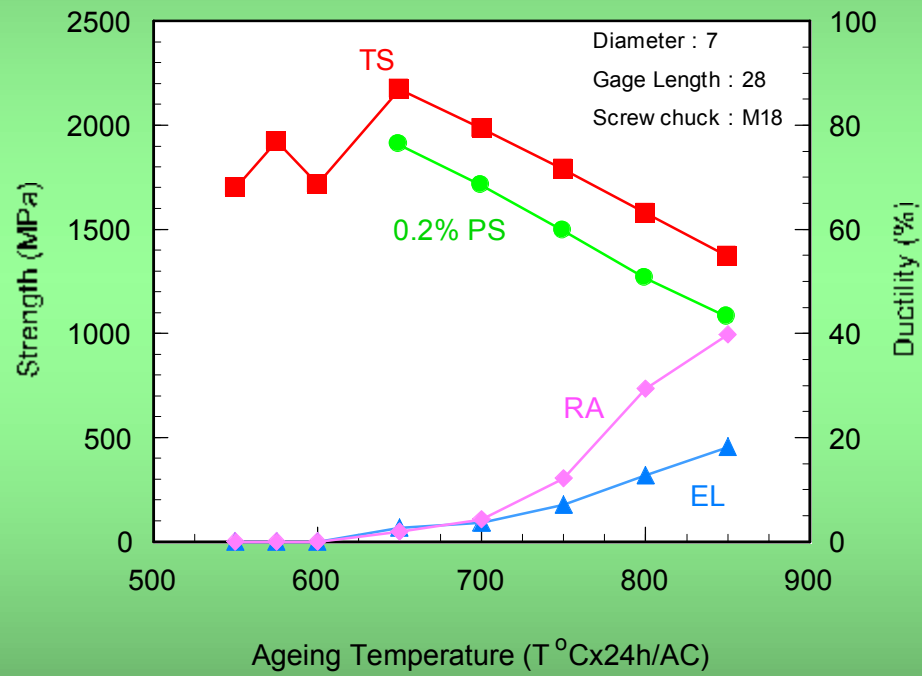


# Ageing Hardness

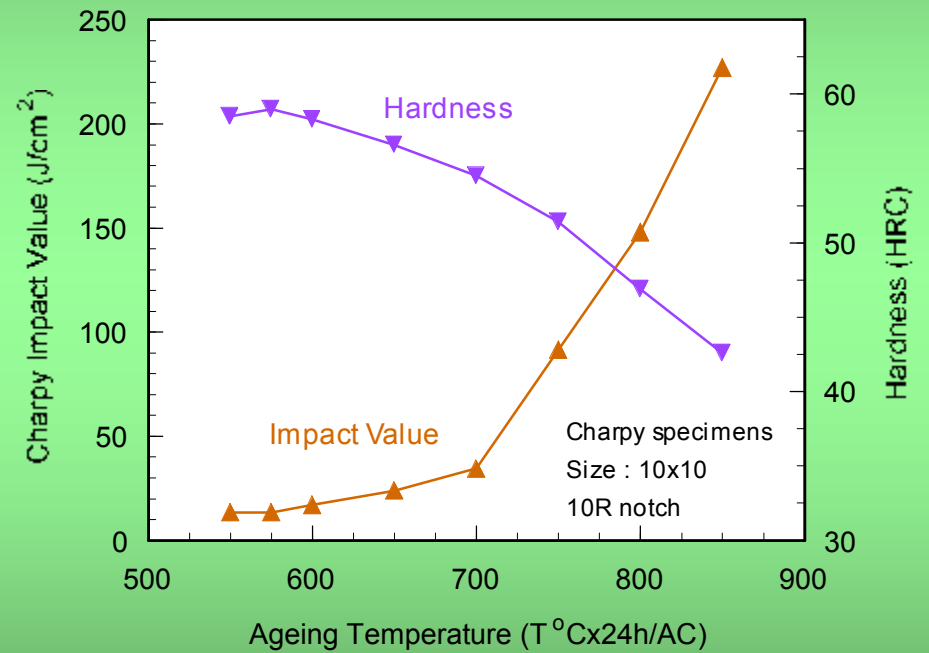


# Mechanical Properties at R.T.

## Tensile properties



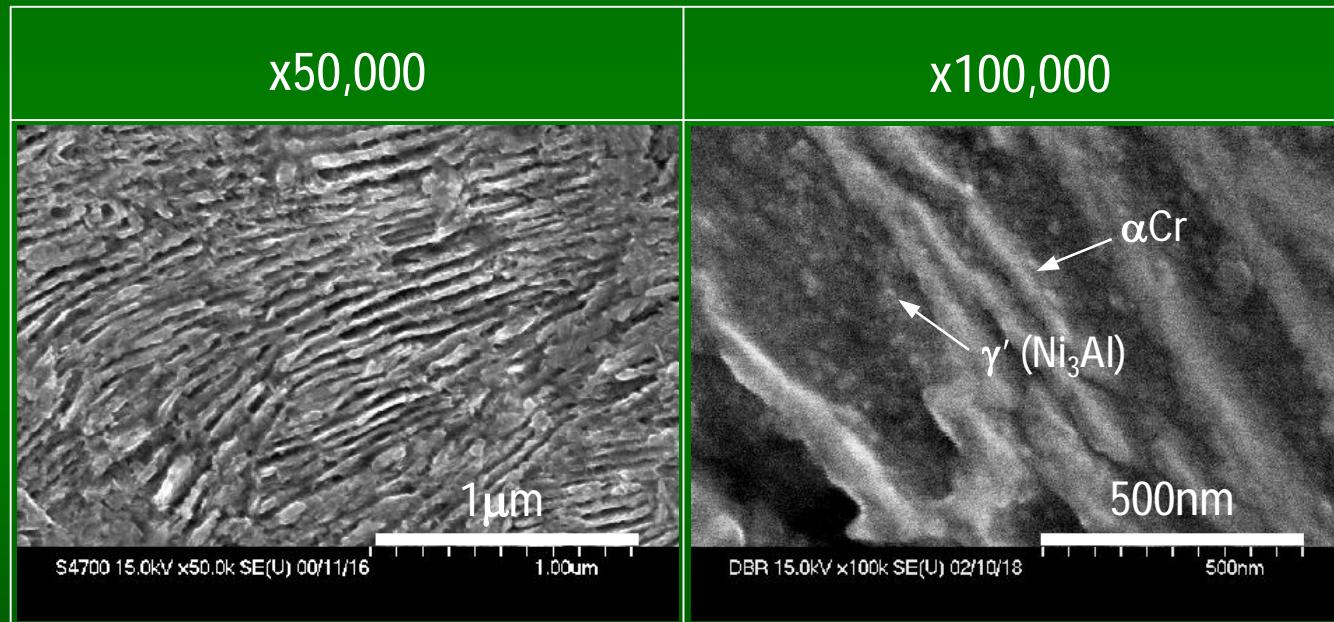
## Charpy Impact Value



# Microstructure after ST-AG

## SEM images

Solution treatment (ST) : 1150deg.C x over0.5hr / WC  
Aging (AG) : 550deg.C x over16hr / AC

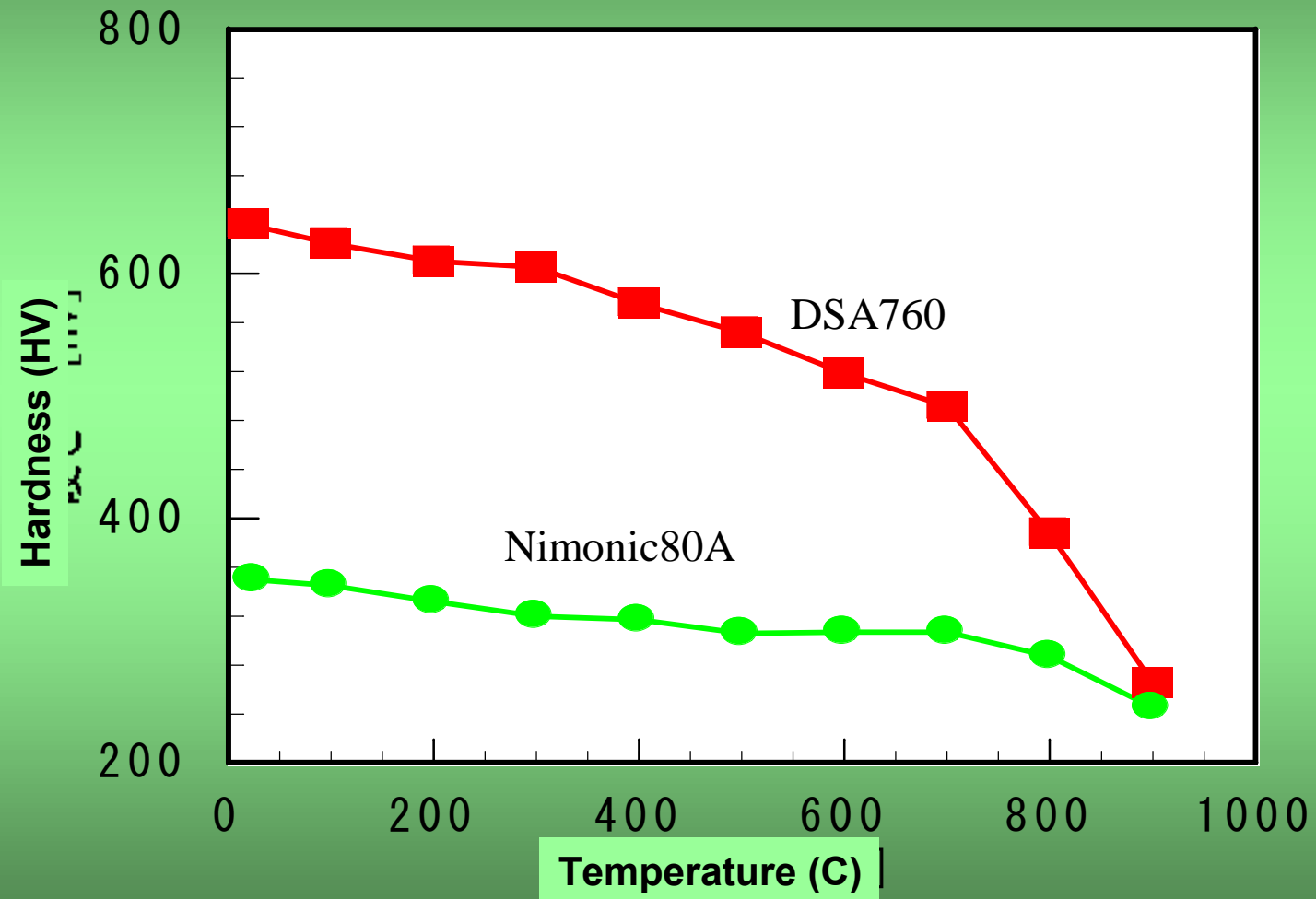


Hard phase consists of lamellar  $\alpha\text{Cr}$  and  $\gamma/\gamma'$  phases

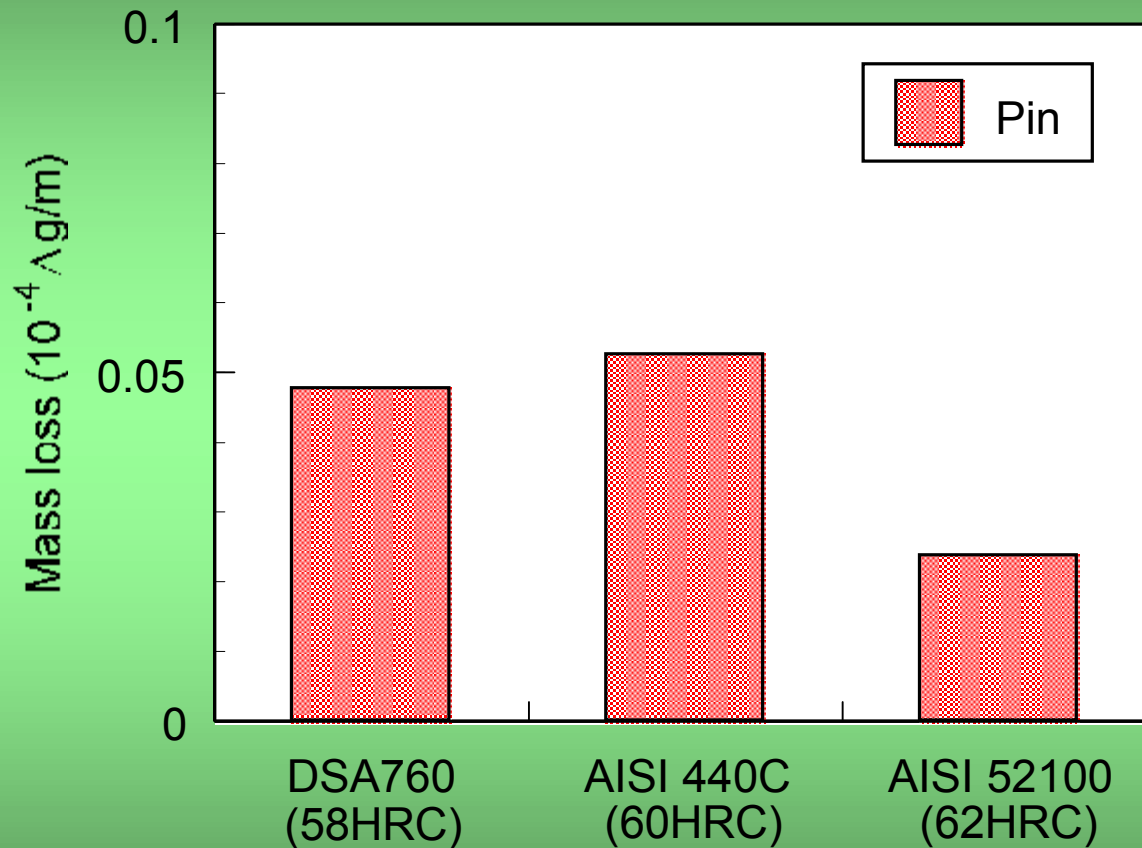
$\gamma'$  :  $\text{Ni}_3\text{Al}$



# Hot Hardness



# Wear Resistance



<Test condition>

Test temperature : RT

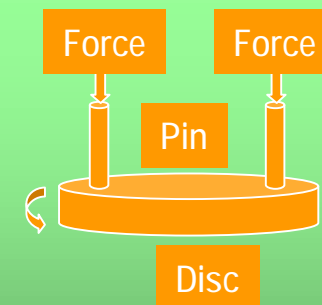
Contact force : 10kg

Distance : 10km

Rev. speed : 1m/s

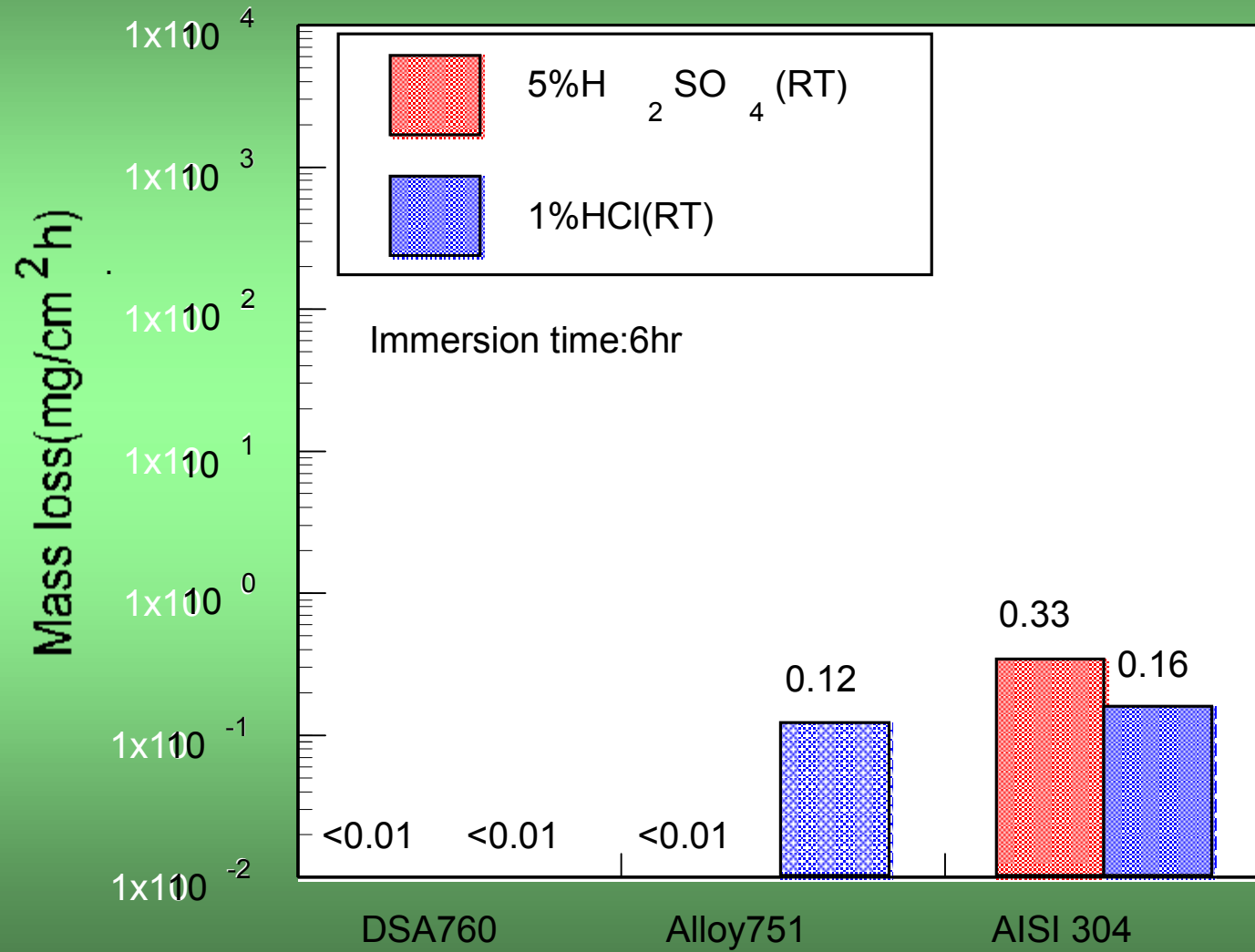
Lubricant : dry

Partner disc : AISI 52100  
(62HRC)



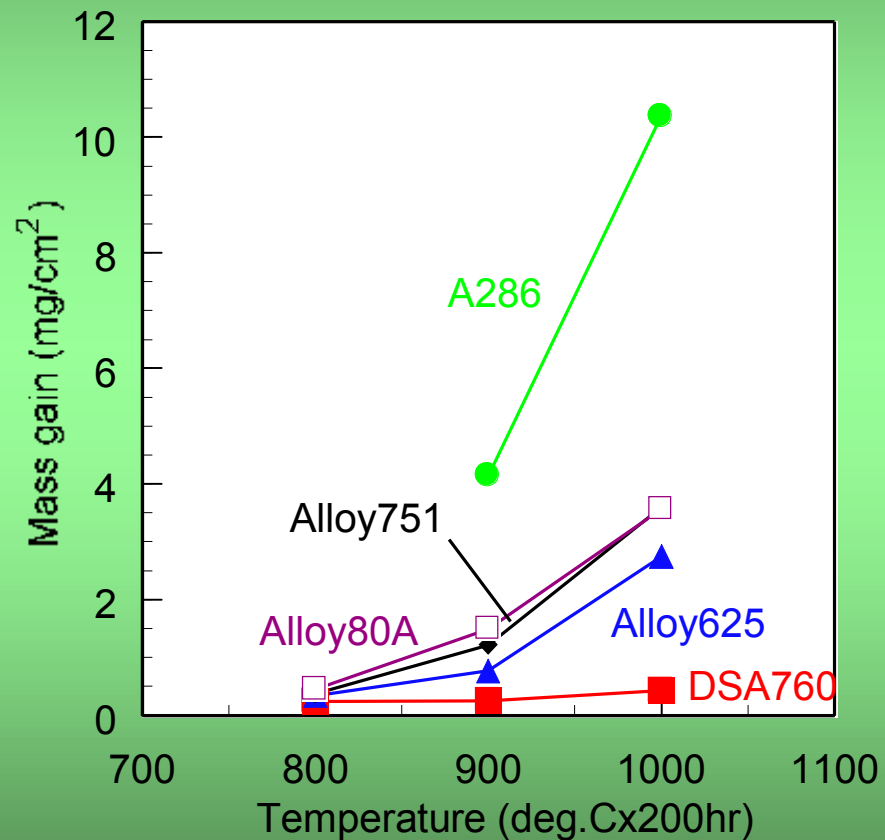
Pin-on-disc wear test

# Acid Corrosion Resistance

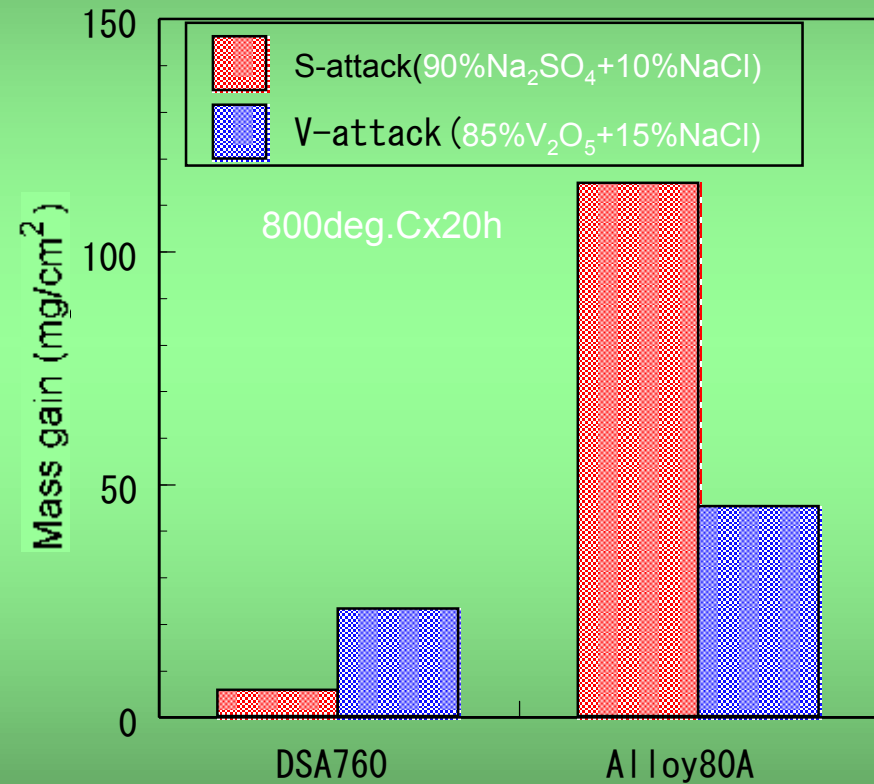


# Hot Corrosion Resistance

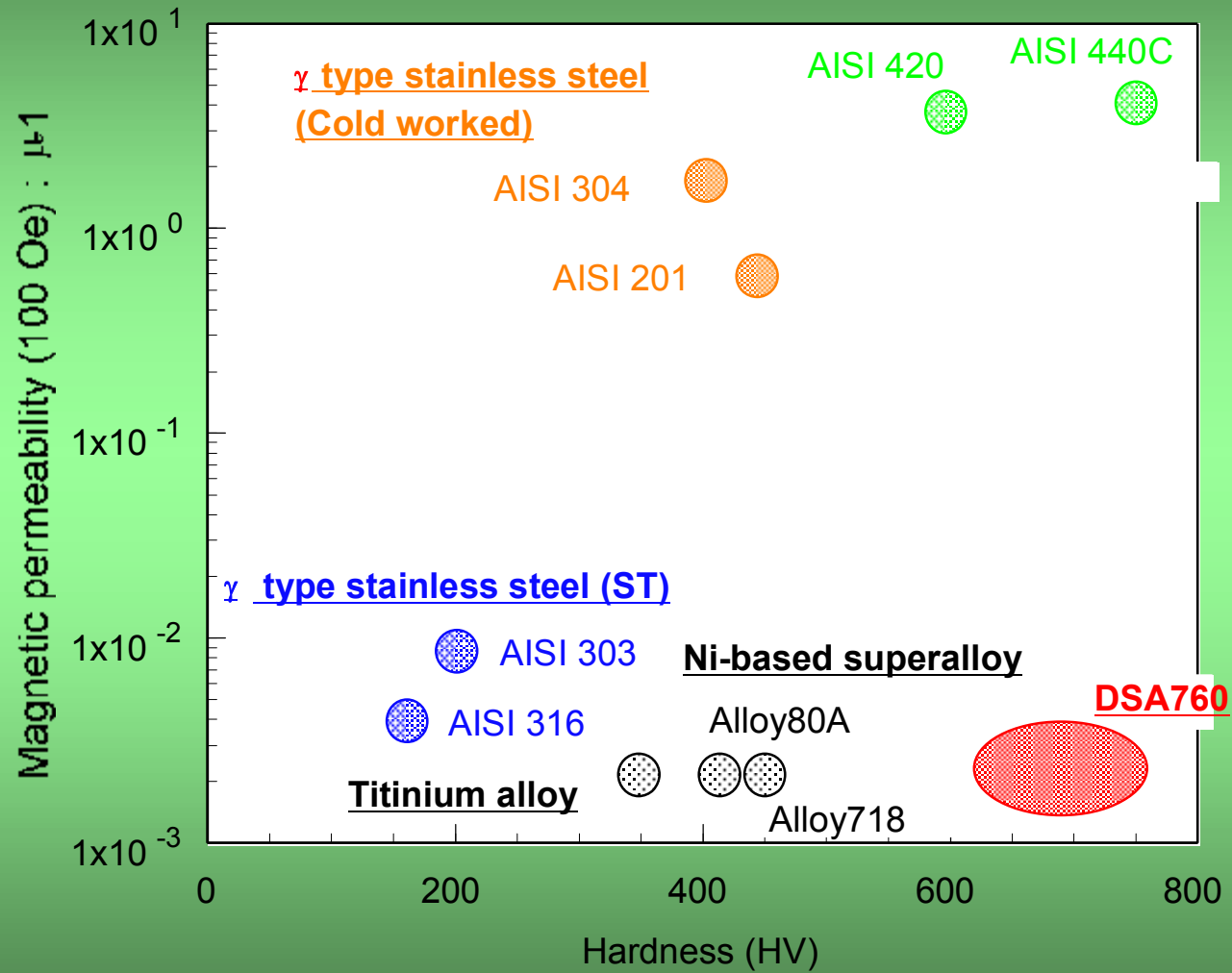
## High temperature oxidation



## Hot corrosion by salt coating



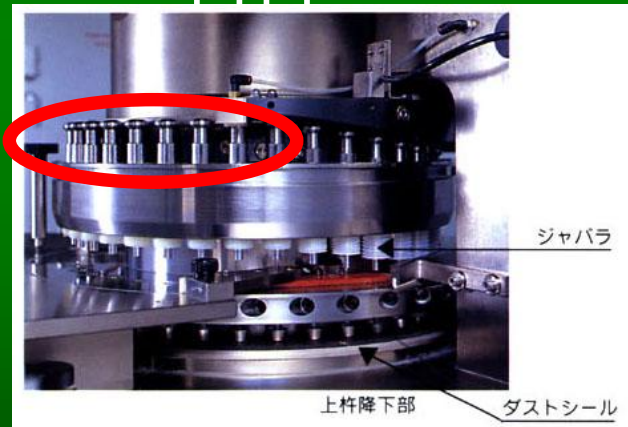
# Hardness and Magnetic Permeability



# Examples of Application (Tools)

- High hardness (High temperature)
- Excellent corrosion resistance

Die tool to  
make drug

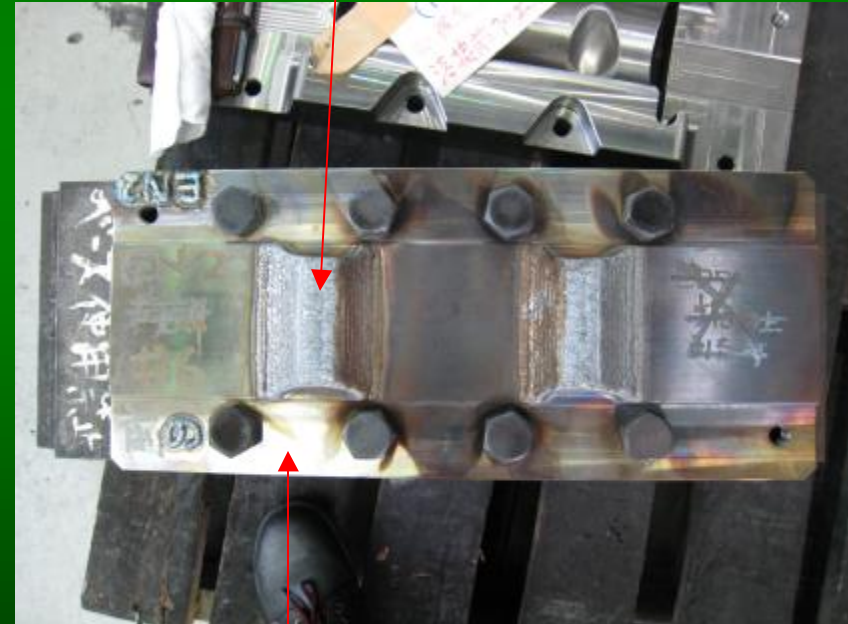


Hot die  
punch



Weld Overlay by DSA760

**Overlay: 55HRC**



**Base: 36HRC**

DAC3

# Examples of Application (Wire, Bearings)

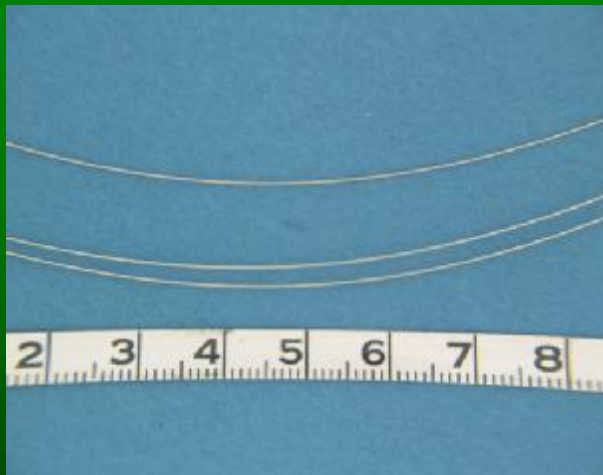
## High Strength Wires

Dot pin, Dental tool

## Non-magnetic Bearings

Magnetic Resonance Imaging System (MRI)

Electromagnetic Clutch



Wire (0.3mm in diameter)



Bearings

Thank you so much for your attention

ARIGATOU GOZAI MASHITA !!

Questions ?