NACE Jubail

Technical Meeting

05-01-2010

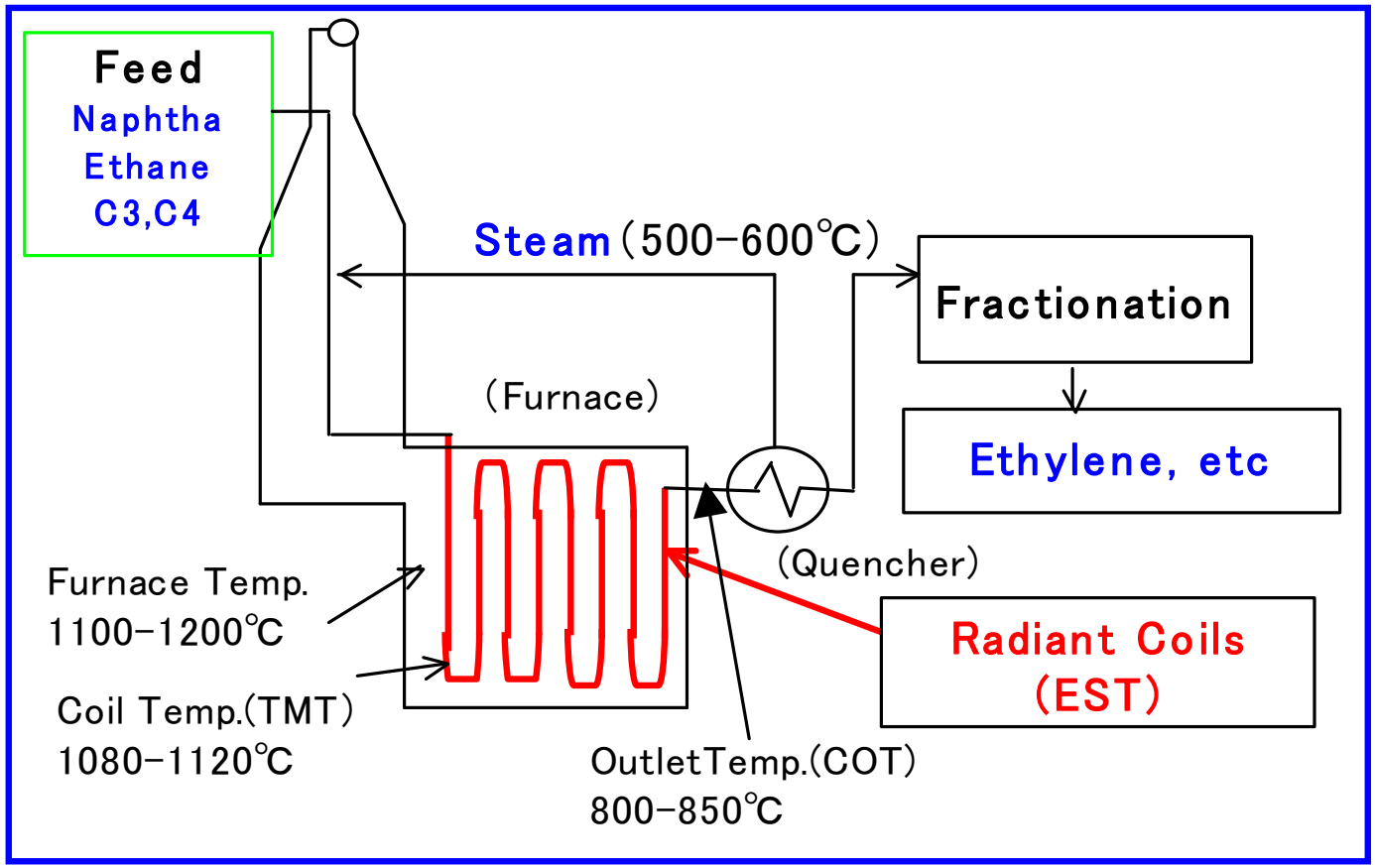
Daido Steel Co.,Ltd

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

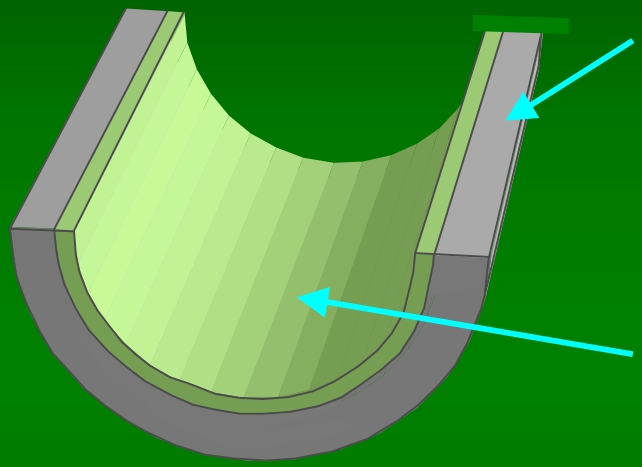
History of radiant coils for ethylene pyrolysis furnace material:

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)

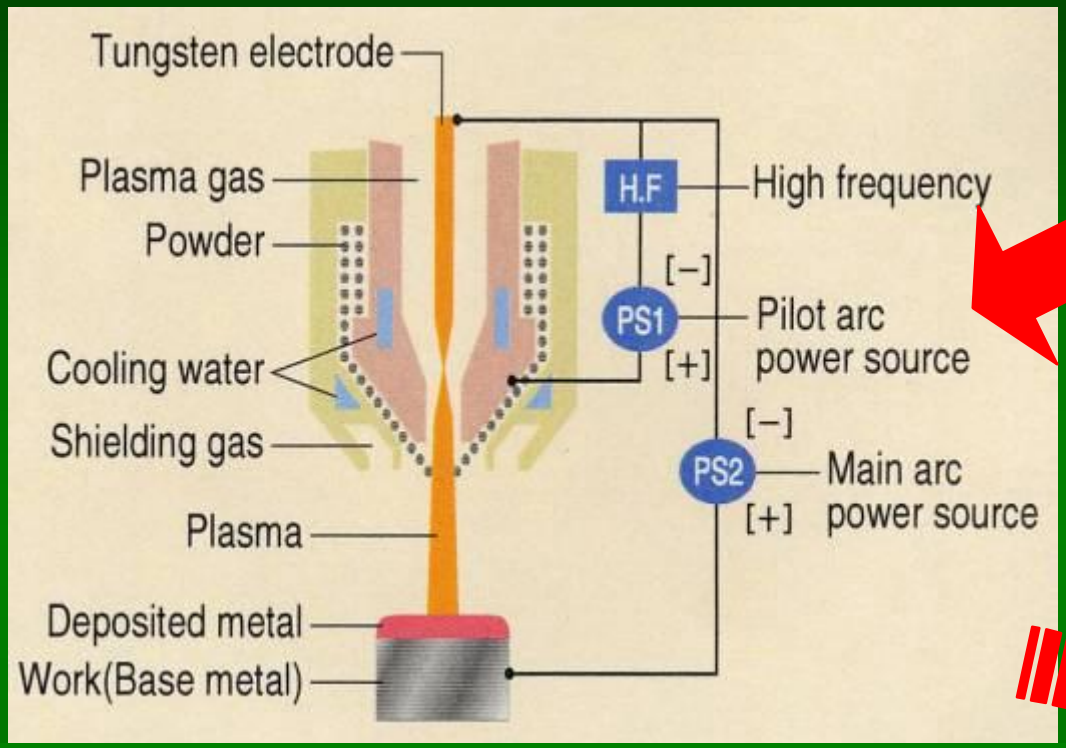
PPW layer

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

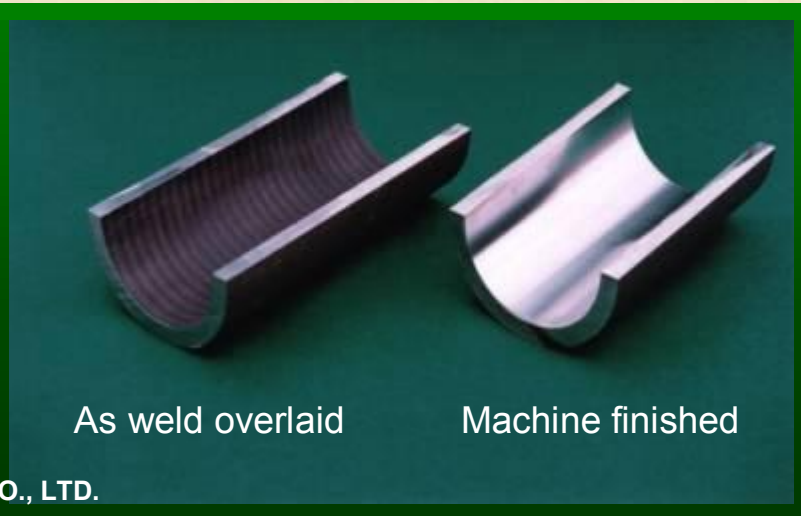
Main Benefits

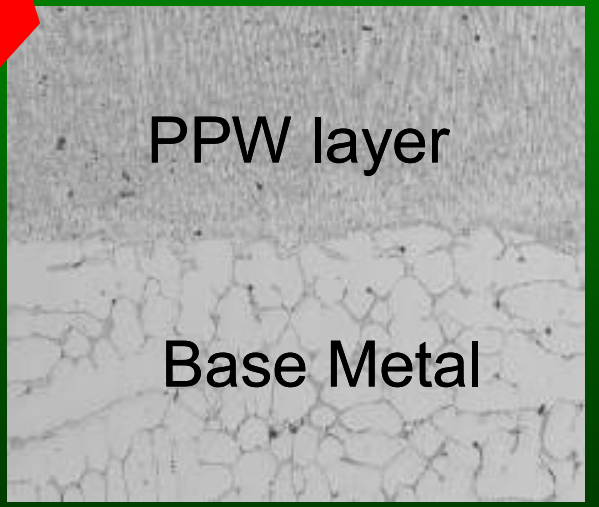
- Anti Catalytic Coke
- Anti Carburization

PPW (Plasma Powder Welding)



Gas atomized 45Cr-50Ni-1Mo powder





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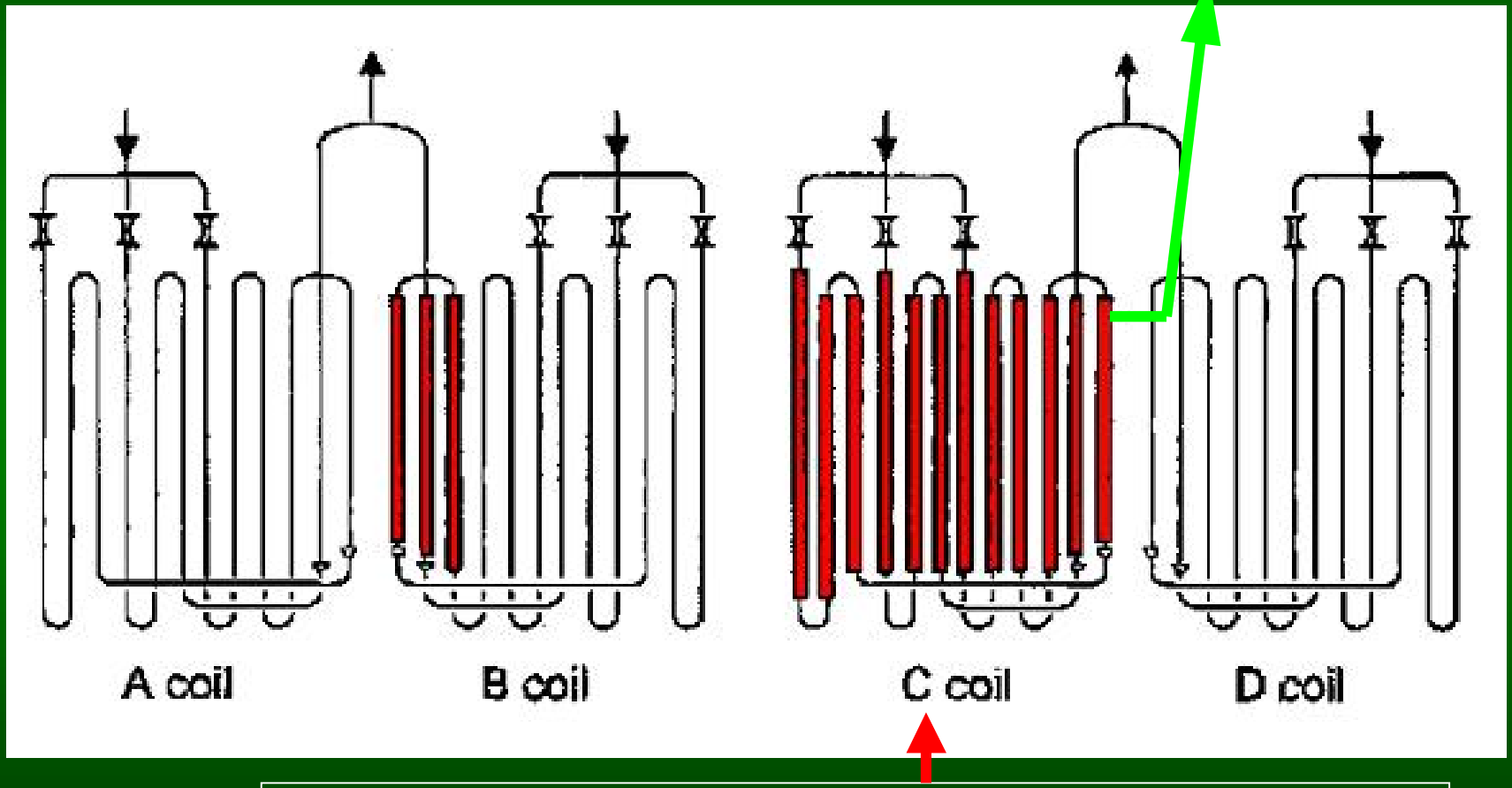
Anti-Carburization

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

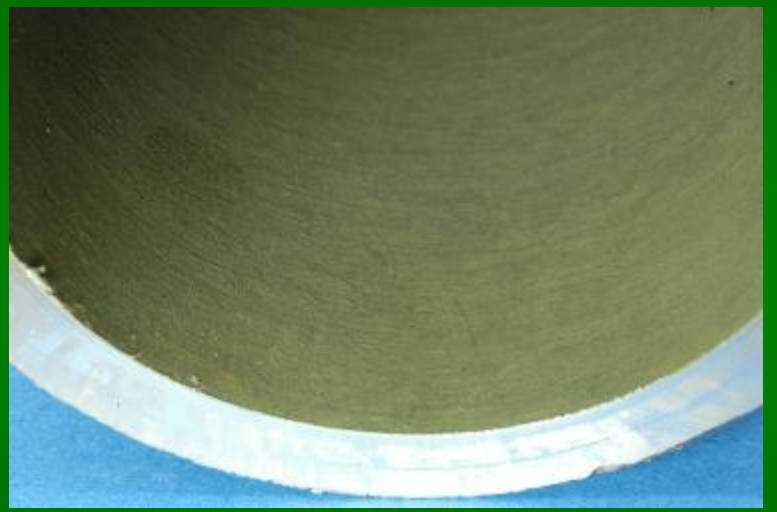
Furnace A: Naphtha Feed

Samples taken after 9 years of operation



Coils with EST have been used since 2000.

Appearance of EST (After 9 years)

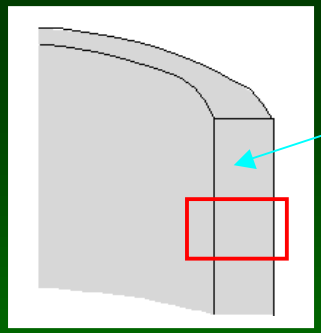


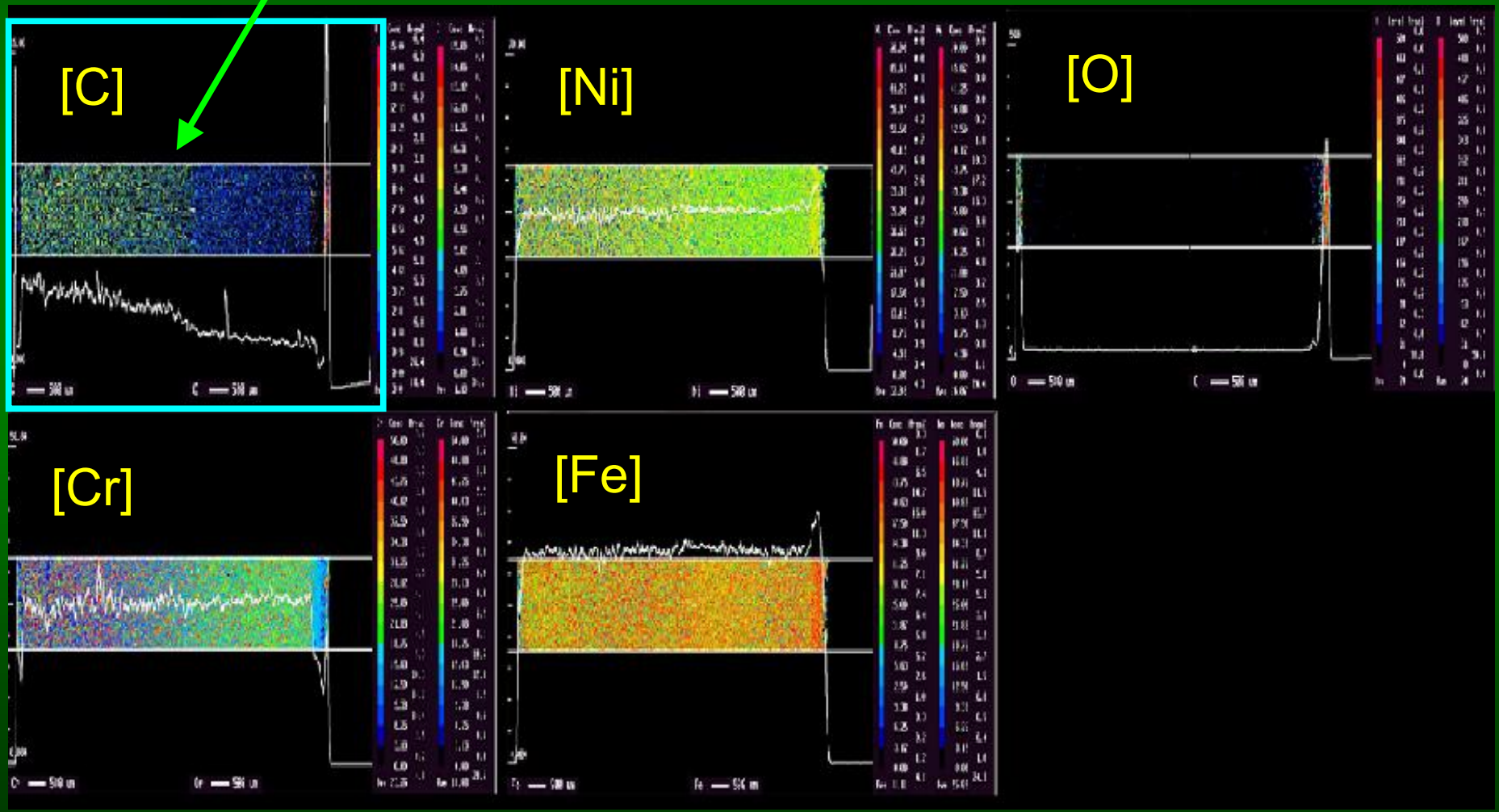
- Green colored surface is recognized. (same as the sample after 24 months)
- No-erosion or damage is observed.

Cross Section Composition Analysis

HP-Nb, after 2 years of operation

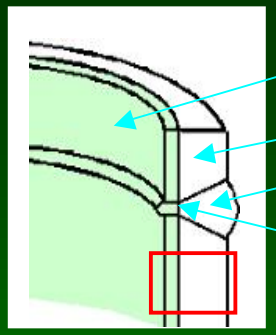
- Fully carburized.
- [C]: 4.7% (ID), 1.1% (OD)

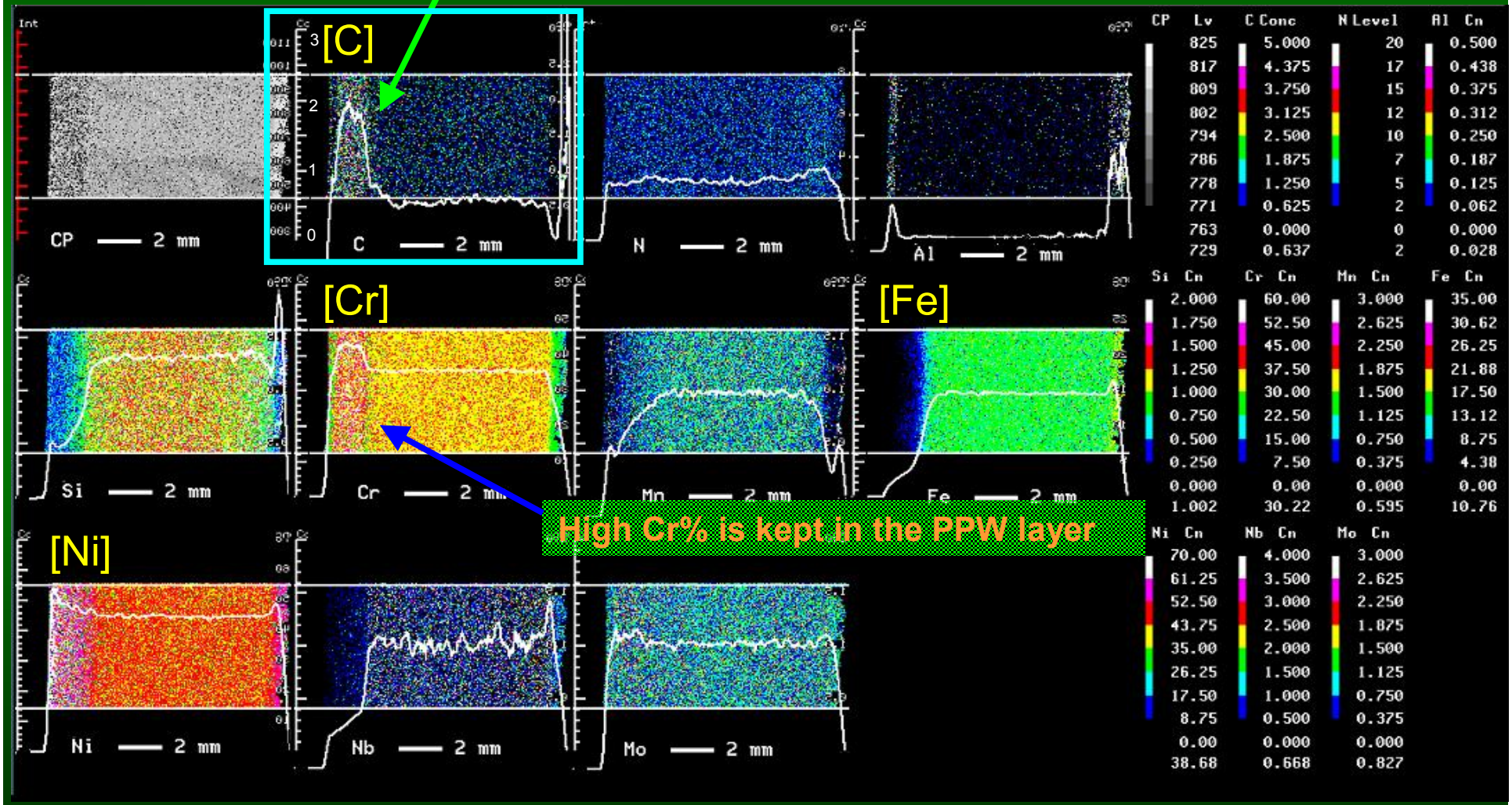




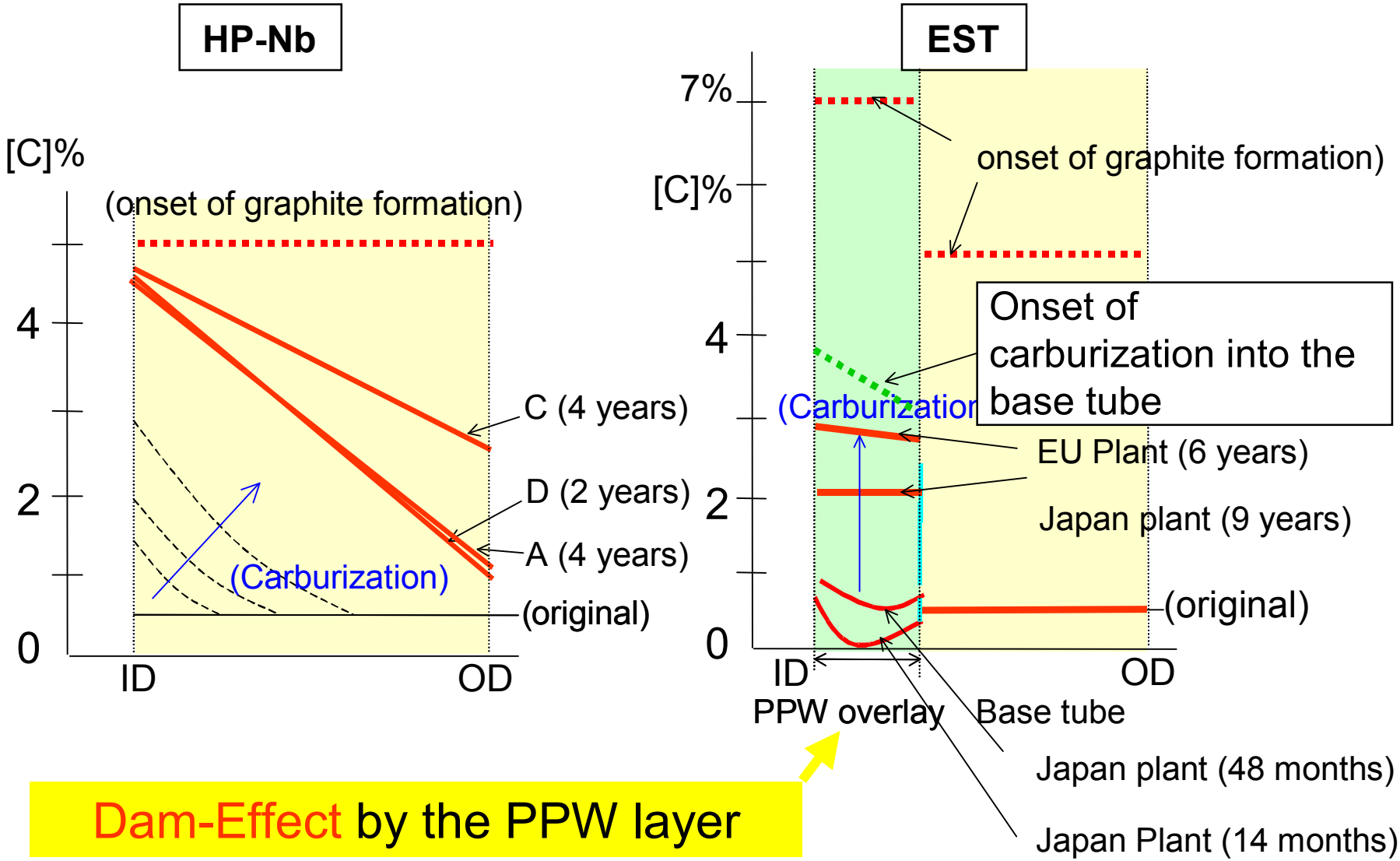
Cross section composition analysis
EST, after 6 years of operation

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



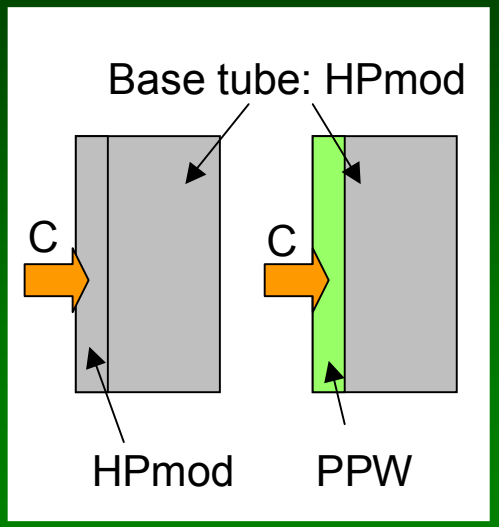


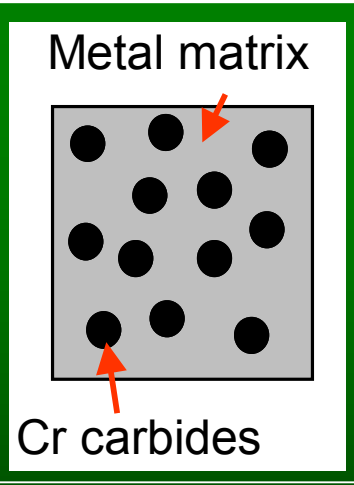
Actual Carburization Comparison

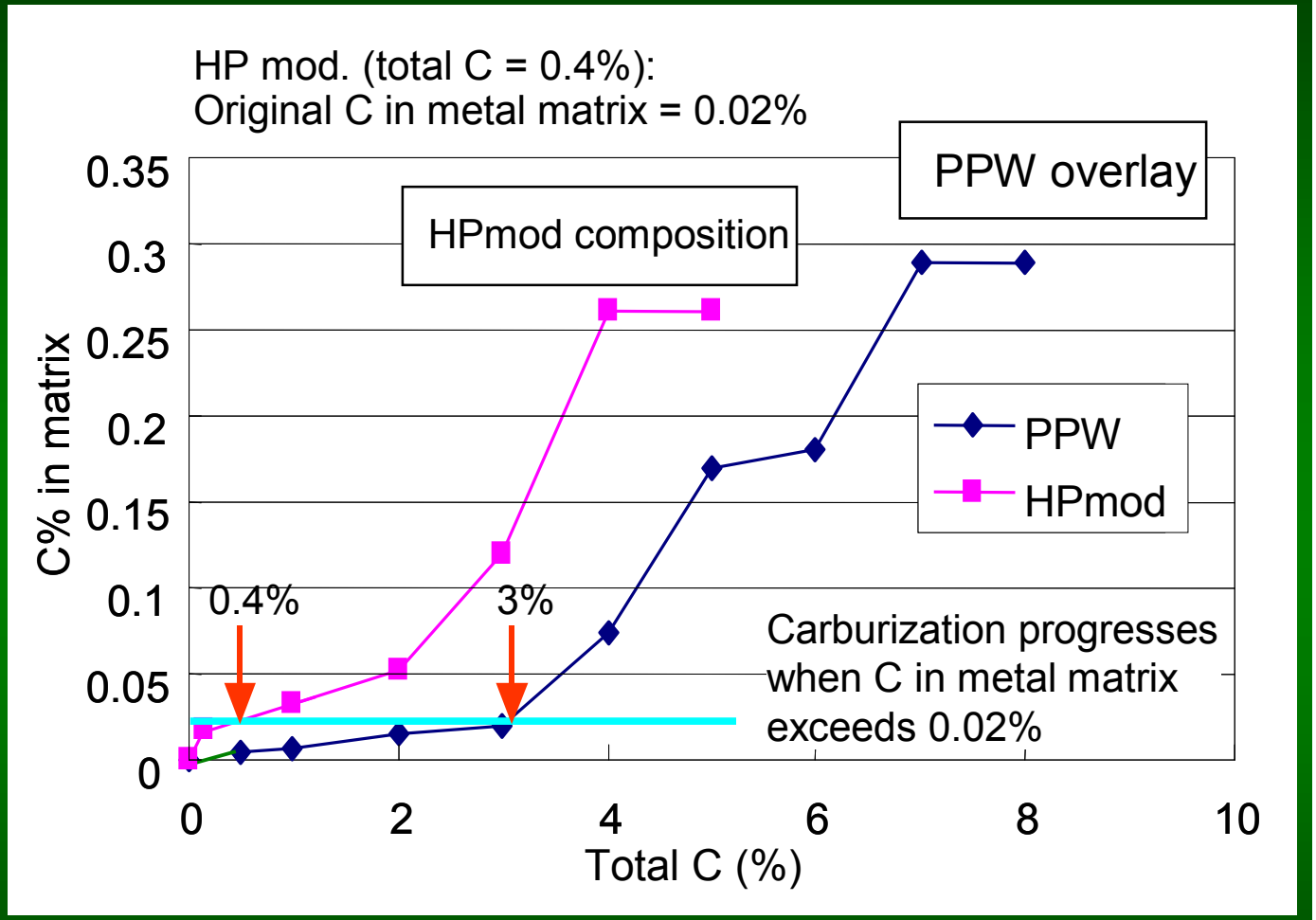


Dam-Effect by the PPW layer

Mechanism of Dam-effect







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

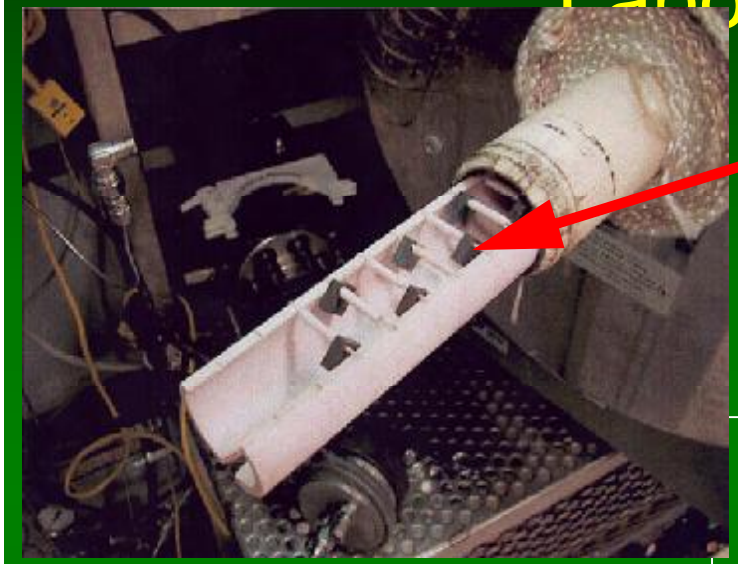
Lack of carburization in EST can prevent physical distortion and help maintain stable operation.

Anti Catalytic Coke

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

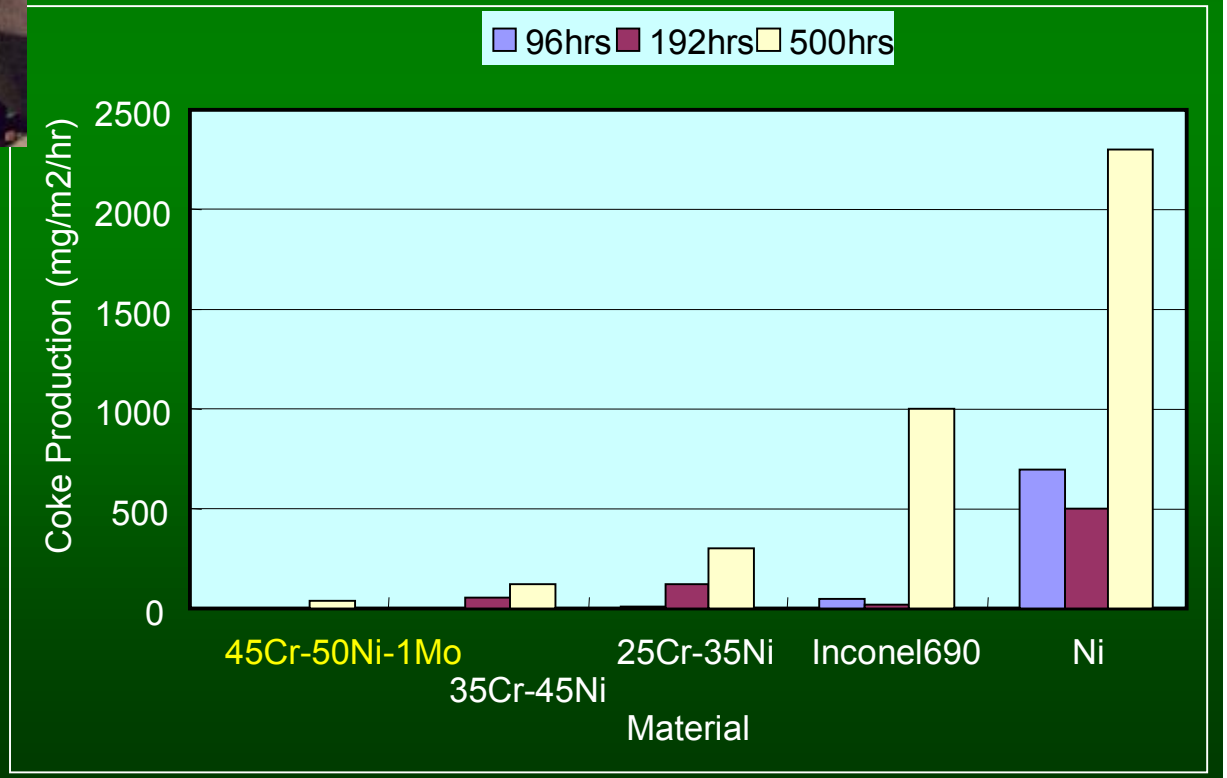
Coke Resistance

Laboratory screening

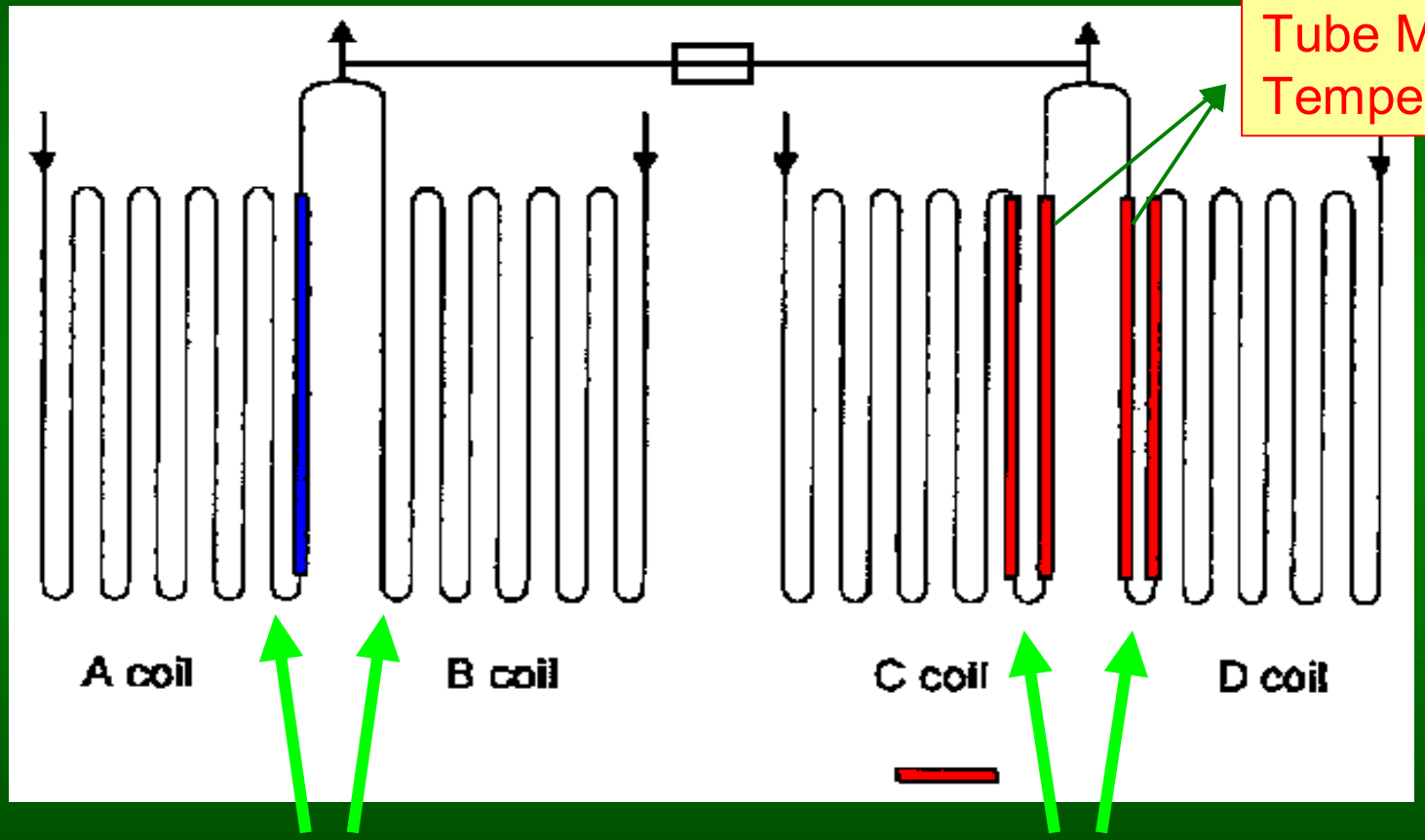


Metal coupons in hot gas stream
accumulate coke as experiment proceeds.
Coupon EST is prepared by PPW process

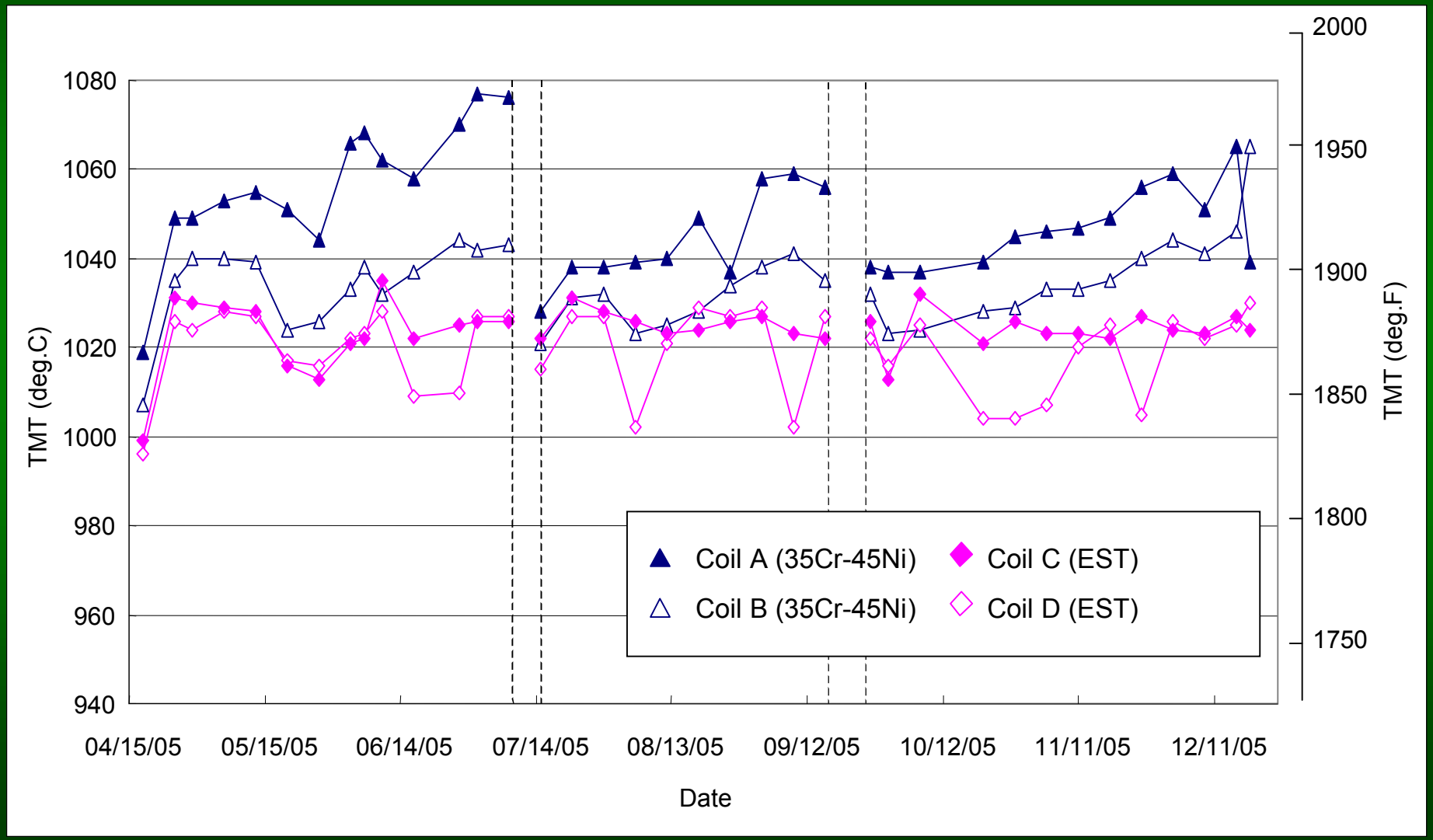
Simulated
process gas
environment



Furnace B: Gas Feed



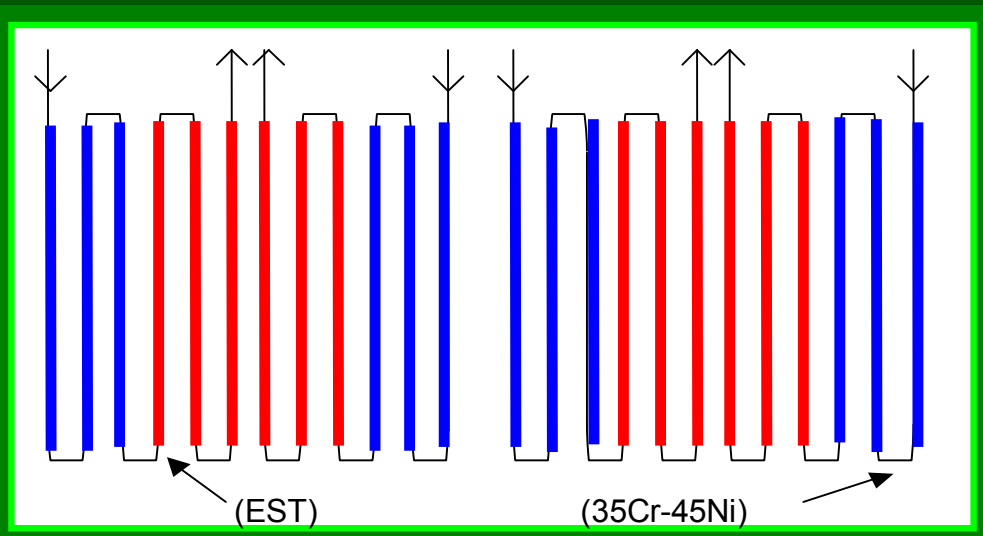
Furnace B: TMT
(Flat means less coke formation)



Furnace C/D: Gas Feed

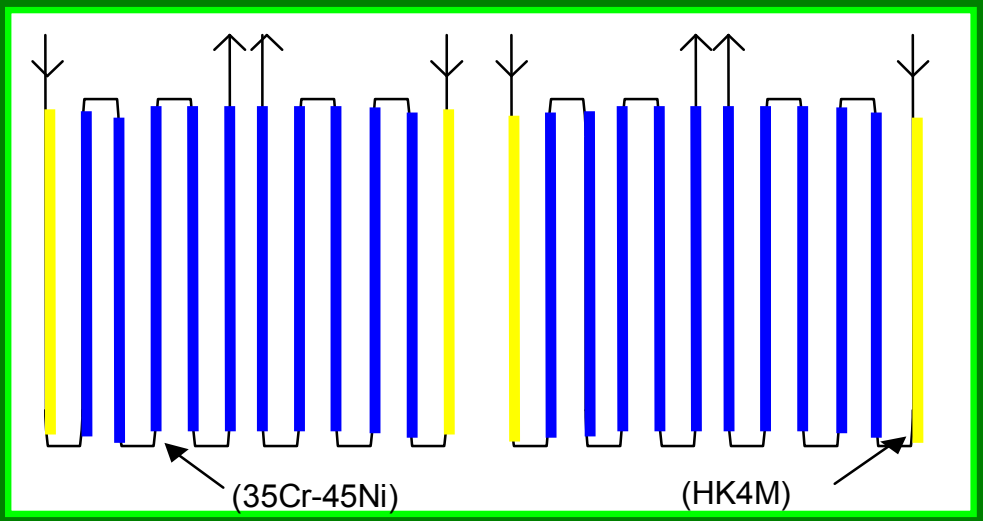
Furnace C:

EST used for 50% of full coil

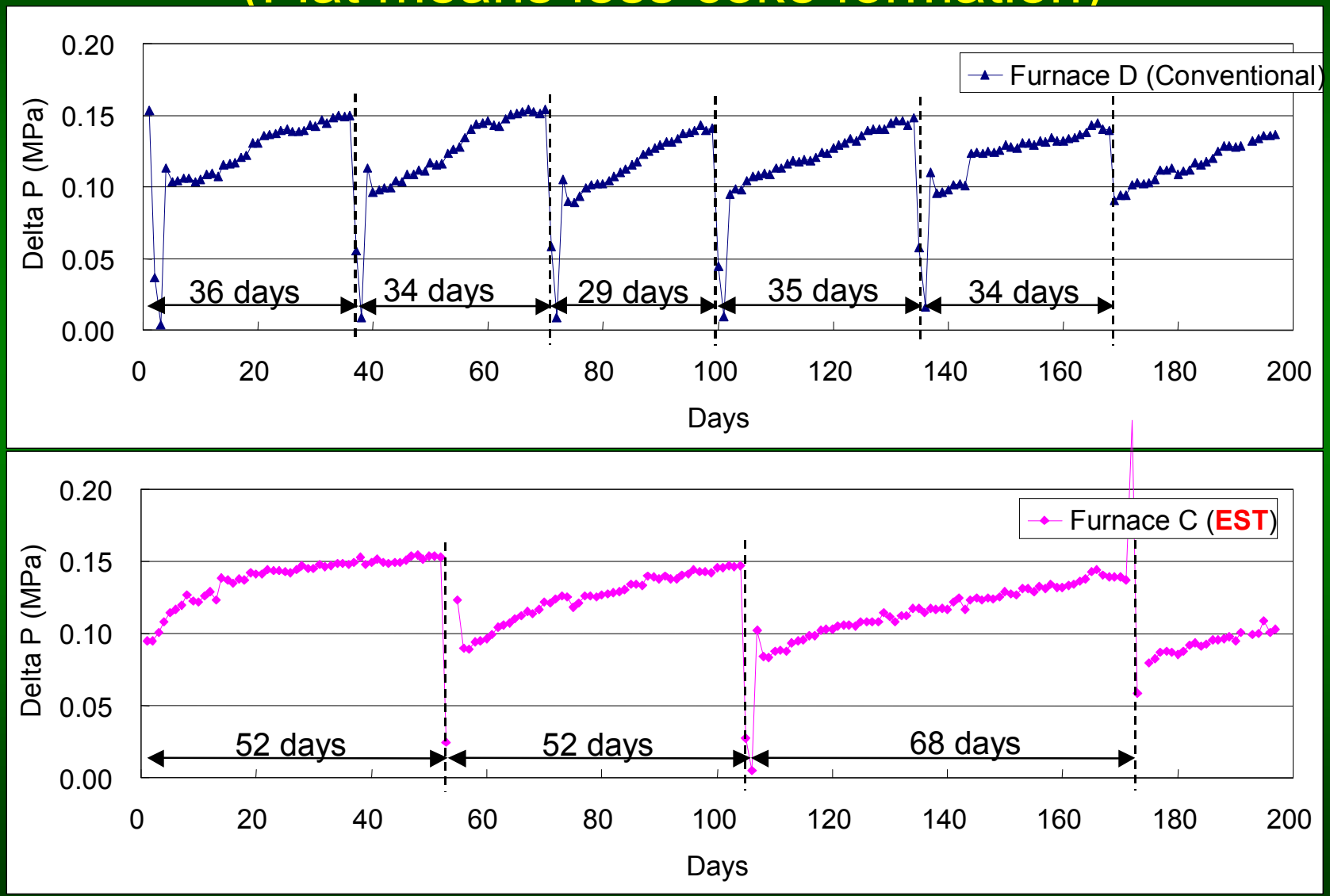


Furnace D:

Identical furnace with 35Cr-45Ni

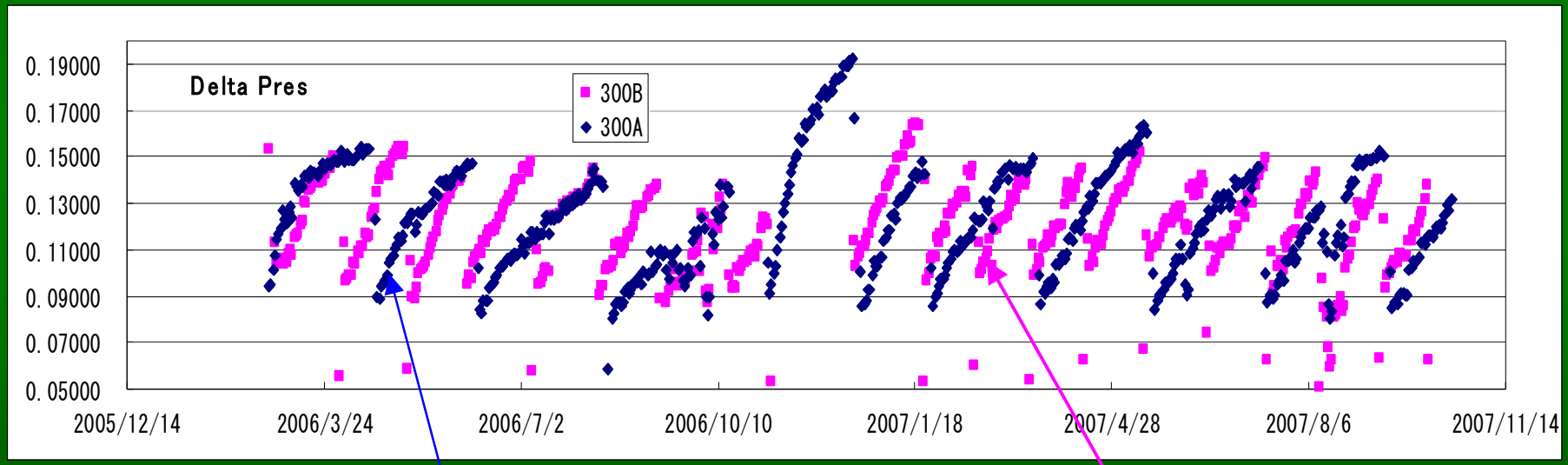


Furnace C/D: Pressure Drop
(Flat means less coke formation)



Lower pressure increase continue through years by "Self Healing Effect" of EST

2 years

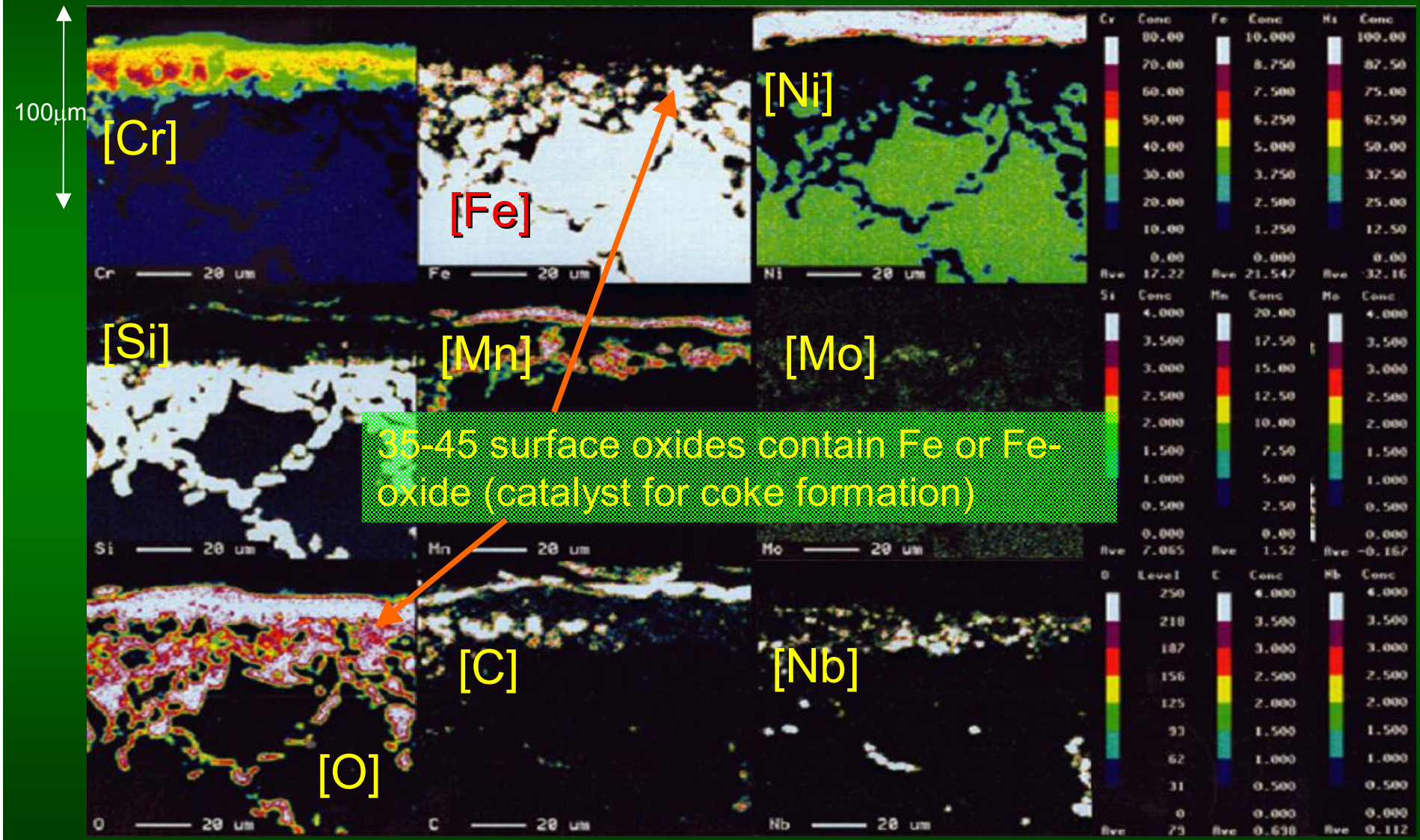


FurnaceC : EST

FurnaceD : 35Cr – 45Ni

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

Near ID surface



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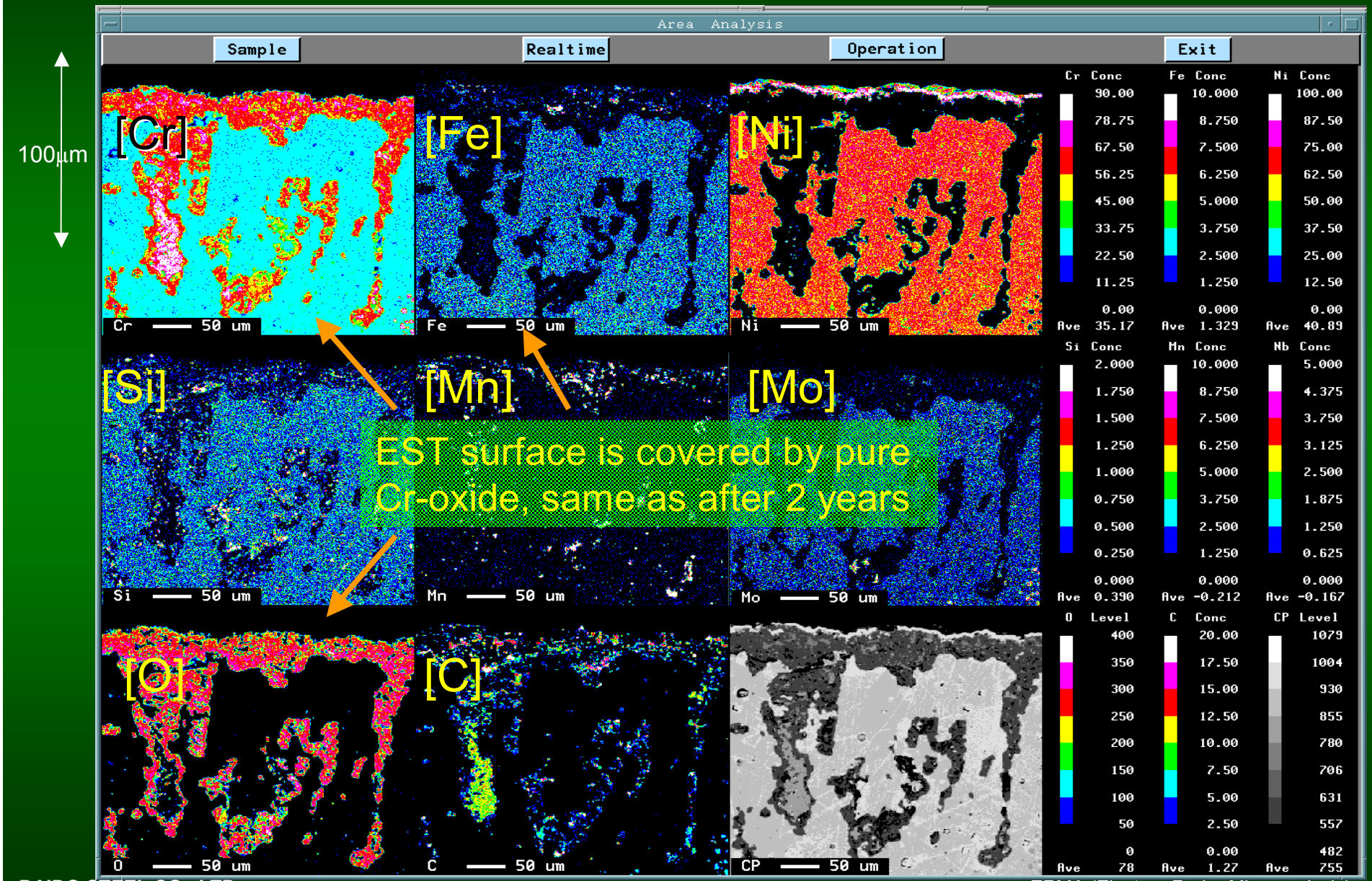
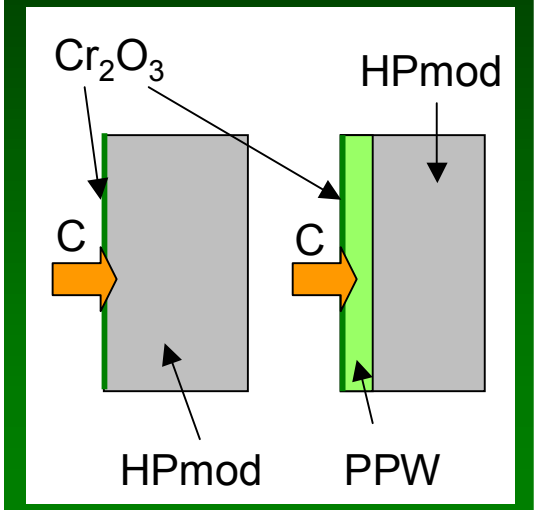
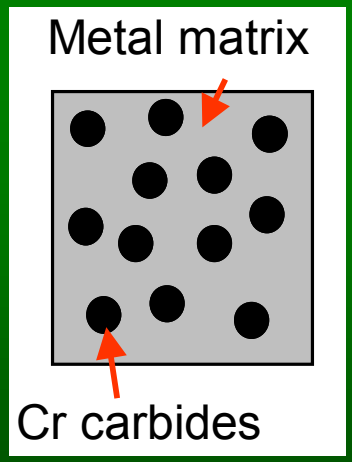
Surface composition mapping of EST after 9 years

Near ID surface

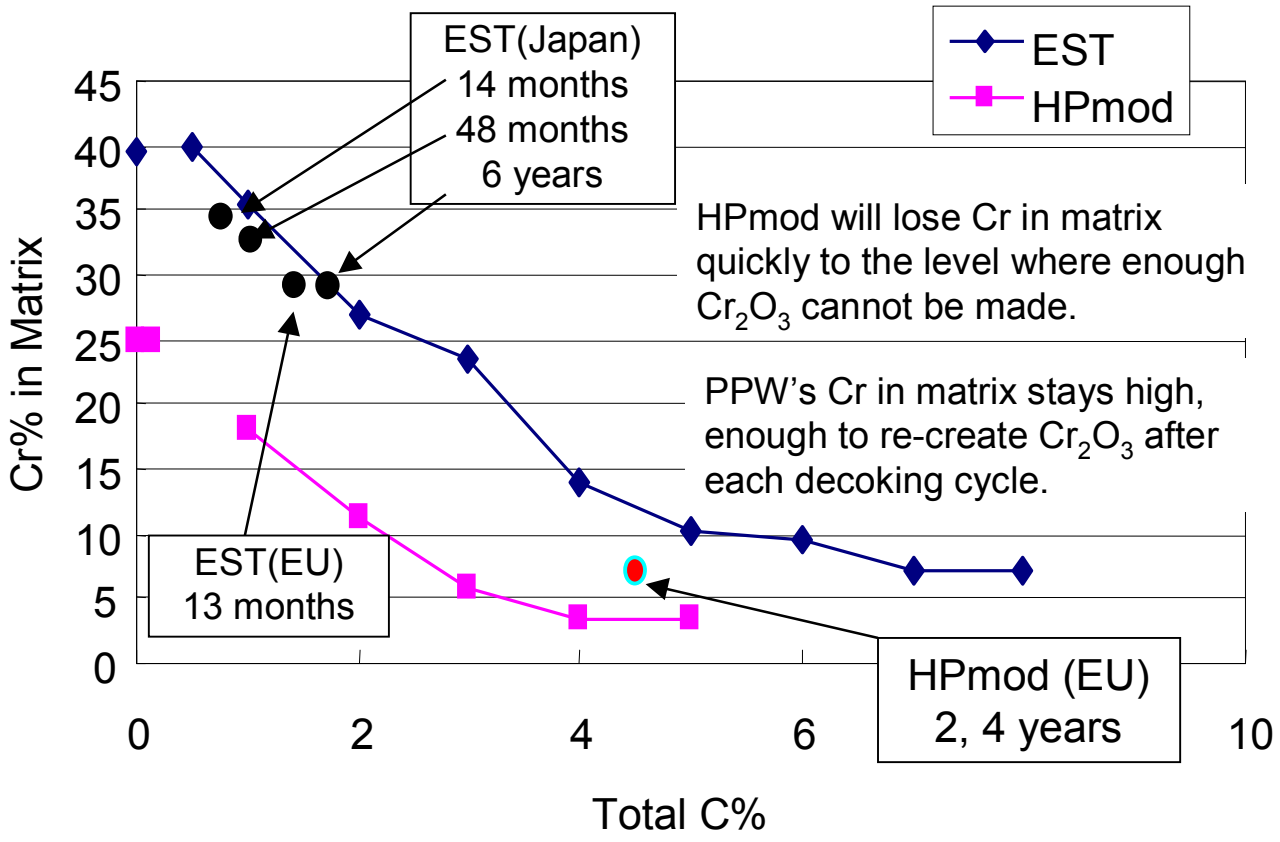


Mechanism of Self-healing





As the alloy is carburized, Cr in metal matrix will be depleted (forming Cr-carbides) and lose the ability to form surface Cr_2O_3.



Due to high Cr in the PPW layer, surface Cr_2O_3 can be re-created and reinforced after each decoking cycle: "Self-healing effect"

Summary

EST has,

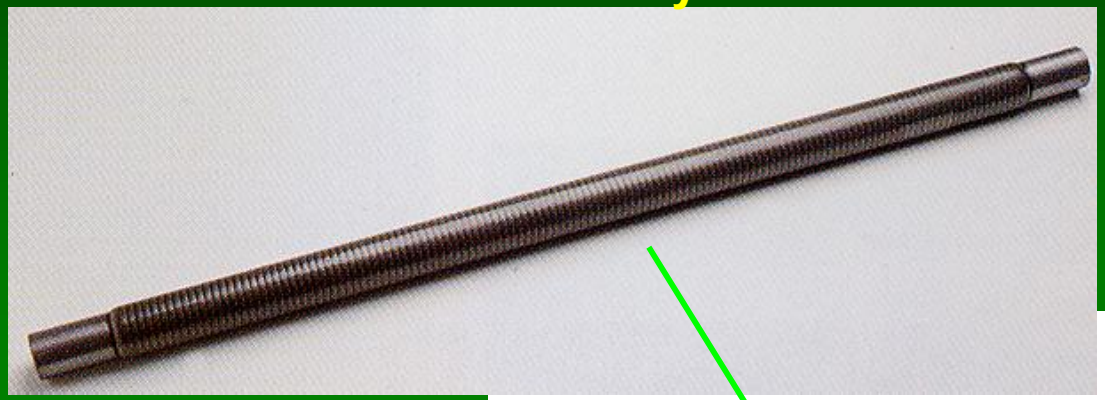
- Extremely high carburization resistance
  - à Extended tube life (Twice or more)
  - à Ability to run at higher severity
  - à Maintained ductility (can survive emergency shutdowns)
- Suppression of catalytic coke formation
  - à Extended run length (Twice in ethane furnace)

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

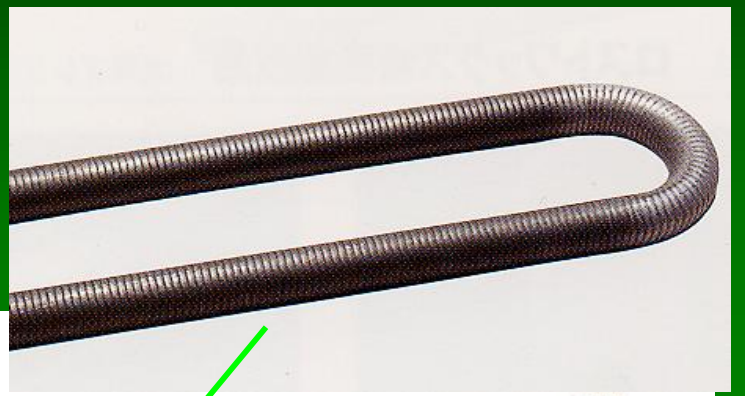
(EST is in operation at over 10 commercial plants)

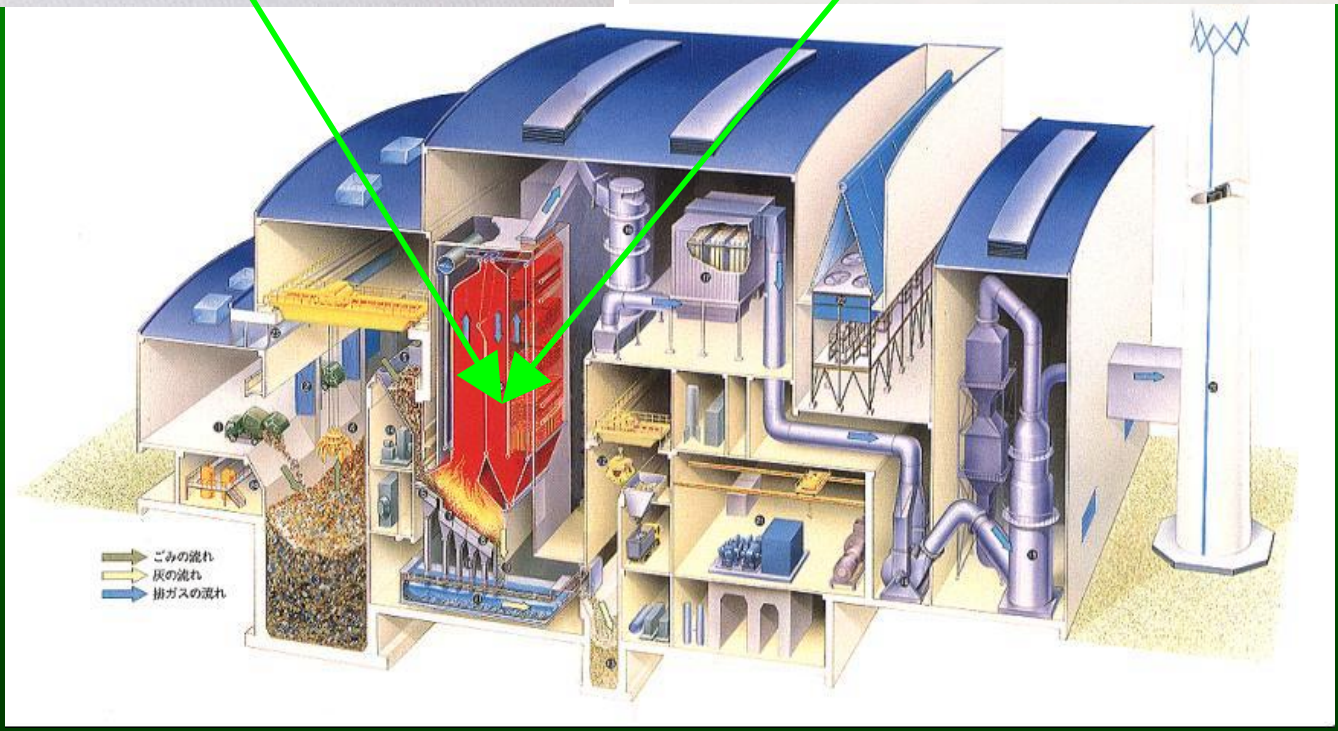
BST (Boiler Super Tube)

Outer surface overlay



Overlay and bending

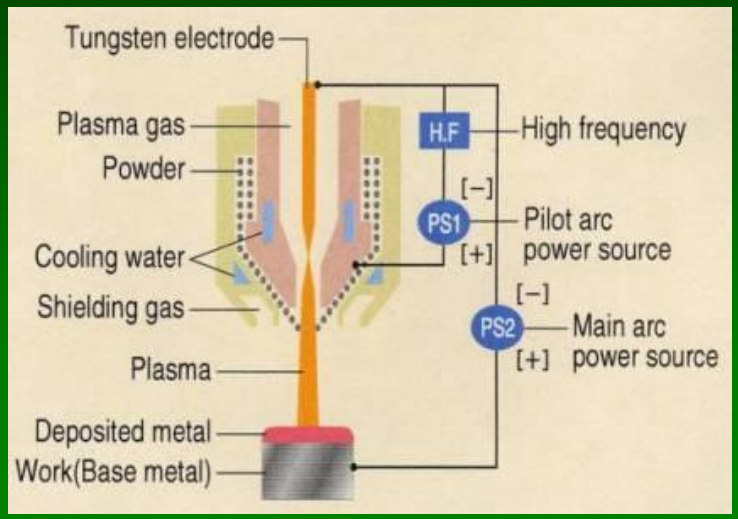




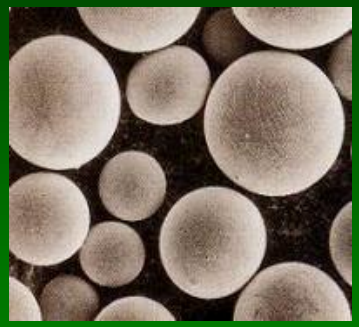
Waste to Energy plant

Benefits of BST (Boiler Super Tube)

Plasma Powder Welding



Original metal powder



BST Production Line

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 1st 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.

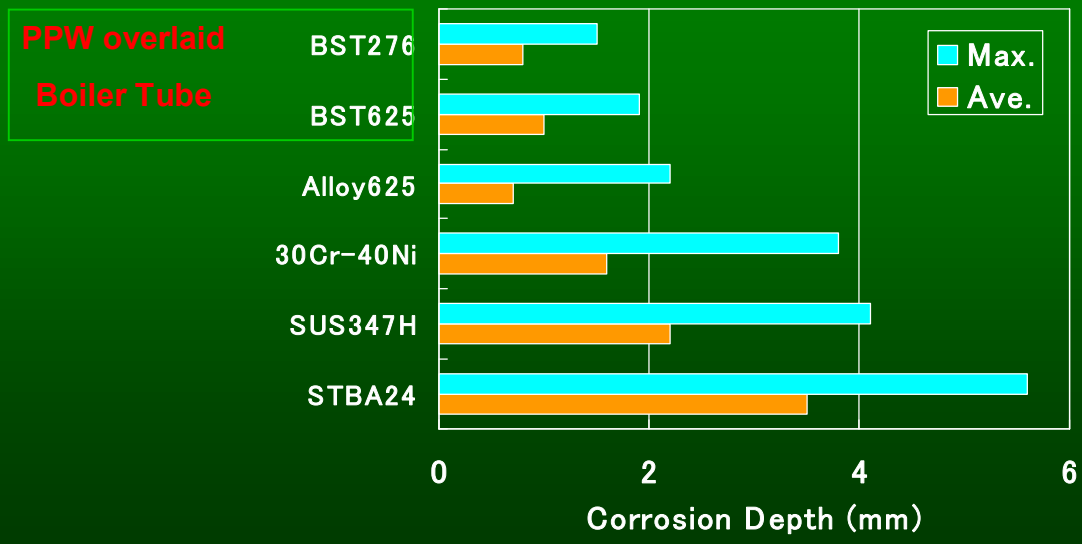
1st generation "BST 276 and BST 625"

(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	El
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: ϕ38.1 - 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

(wt%)

	C	Si	Ni	Cr	Mo	Co	W	Al
BST1	**Ad.**	**Ad.**	**Bal.**	**27**	**-**	**-**	**Ad.**	**Ad.**
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

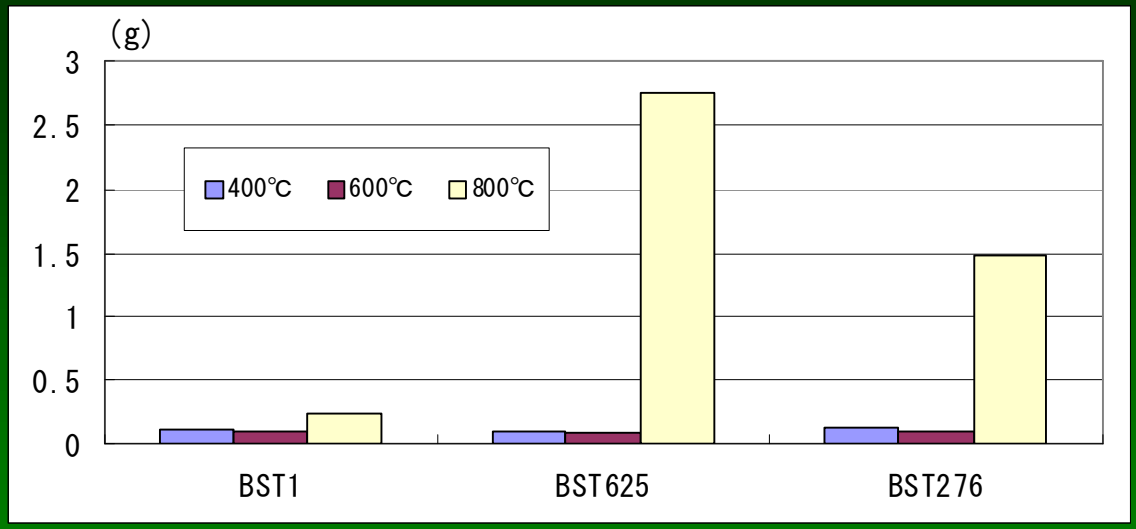
	Mol. %	Wt. %
Na_2SO_4	3	16.8
K_2SO_4	3	20.6
Fe_2O_3	2	12.6
$PbCl_2$	3	28.15
$FeCl_2$	3	12.85
NaCl	2	3.95
KCl	2	5.05

Dipping temperature and time

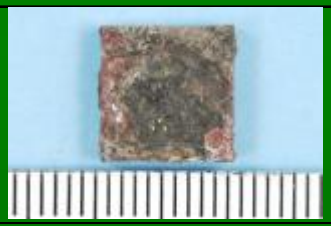
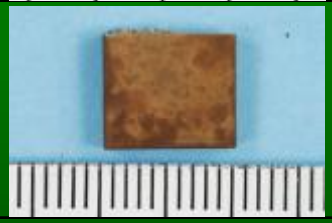
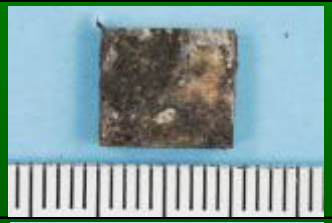
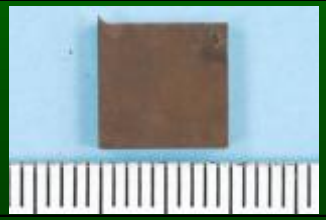
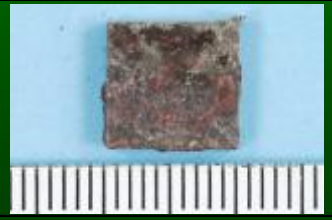
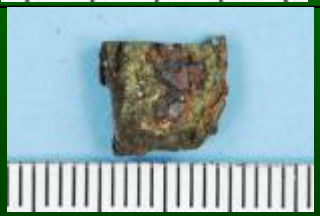
°C	400	600	800
°F	752	1,112	1,472
time	100 hours		

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^{o}C or 1,472^{o}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 αCr and γ' 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.

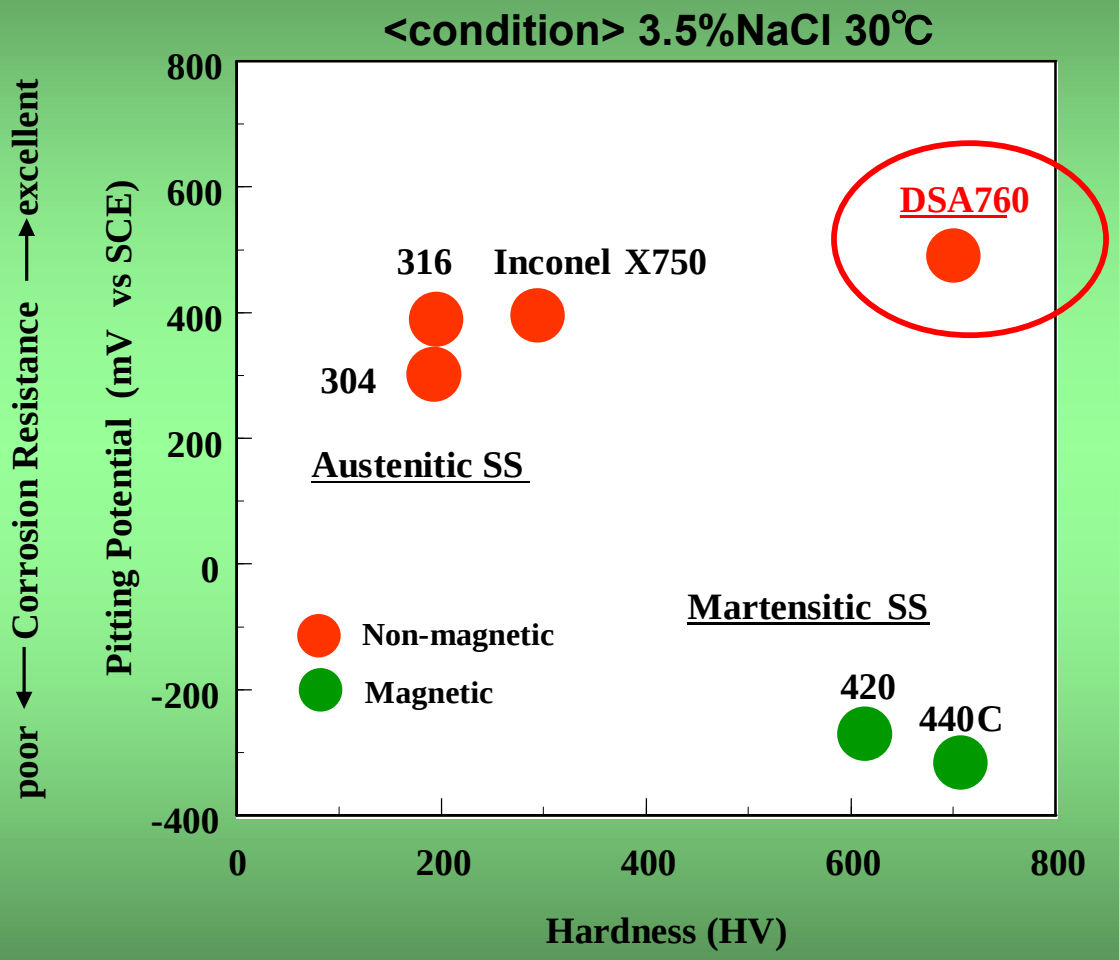
1974 (Russia)
Ni-40Cr-3.8Al was introduced as high hardness and non-magnetic permeability alloy in a Russian paper.

1990 (UK)
Ni-40Cr-3.8Al was introduced again as the Russian Ni alloy and applied to a non-magnetic pressure cylinder.

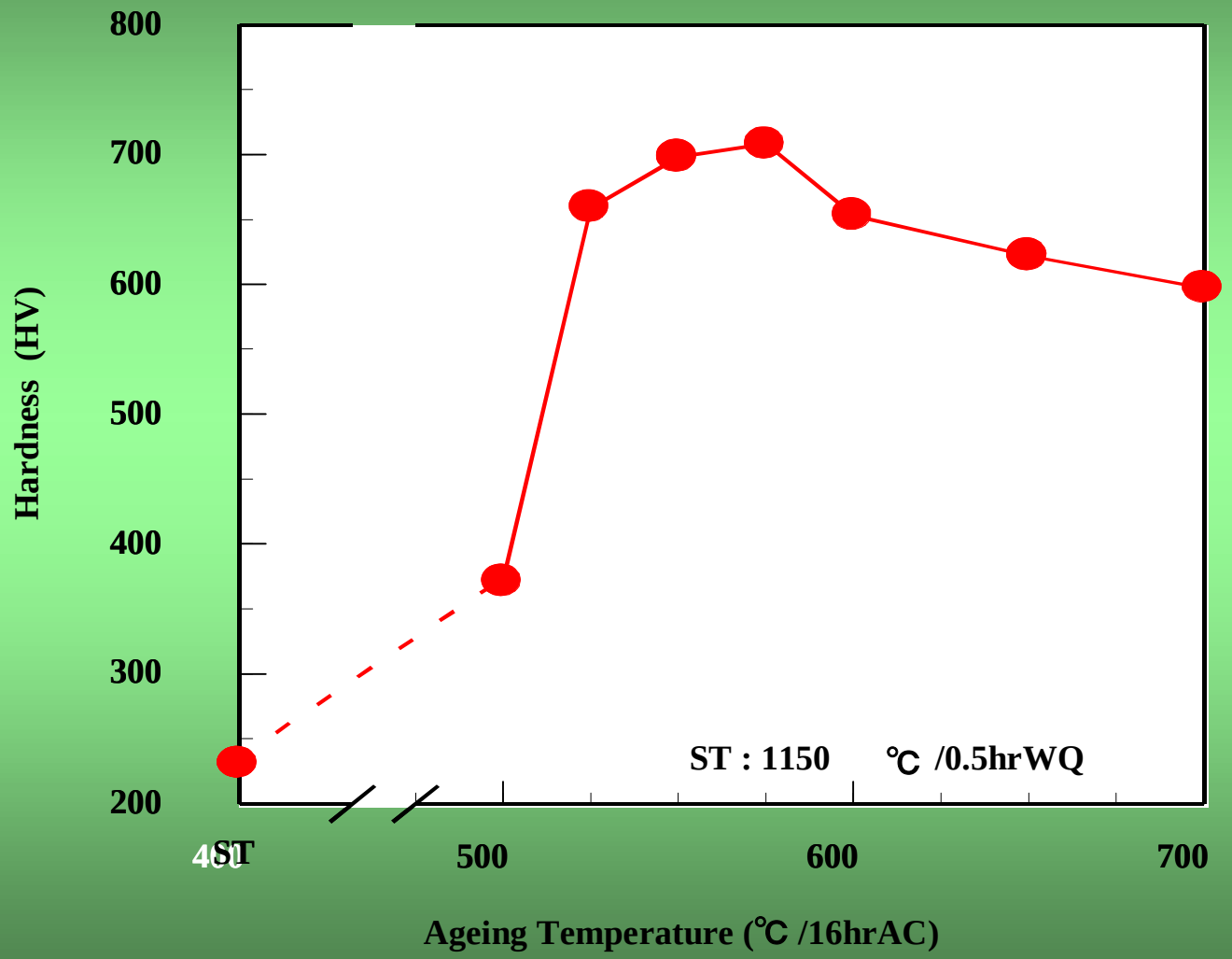
Manufacturing process was cast due to low hot workability.

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

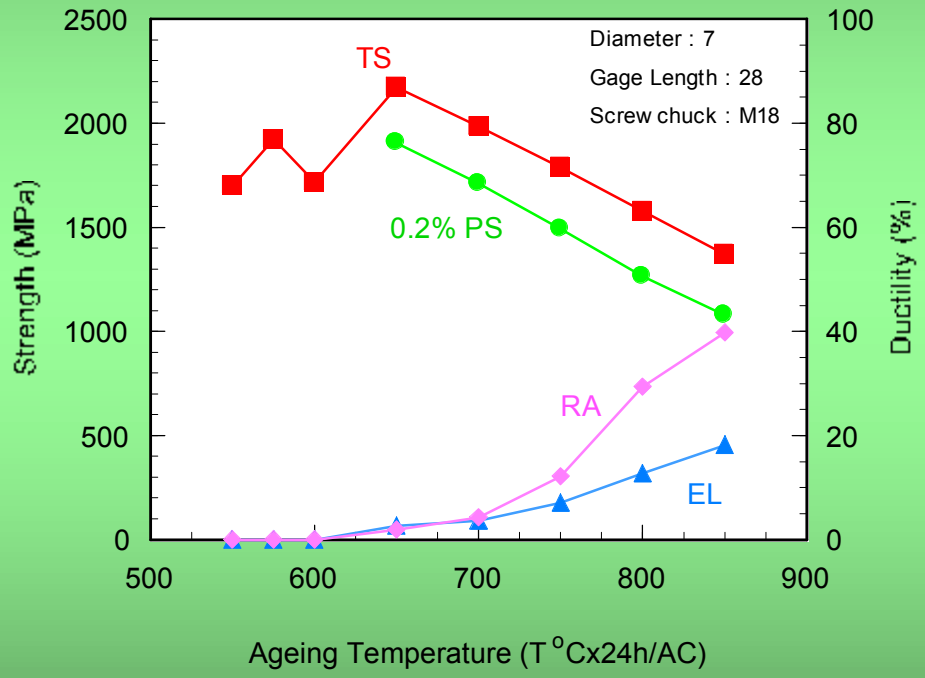


Ageing Hardness

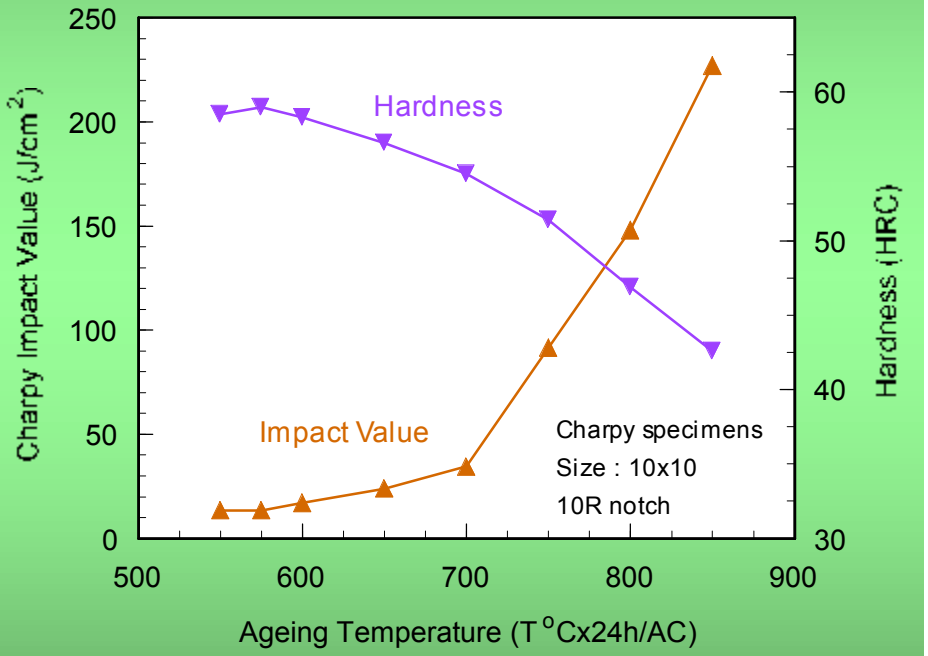


Mechanical Properties at R.T.

Tensile properties



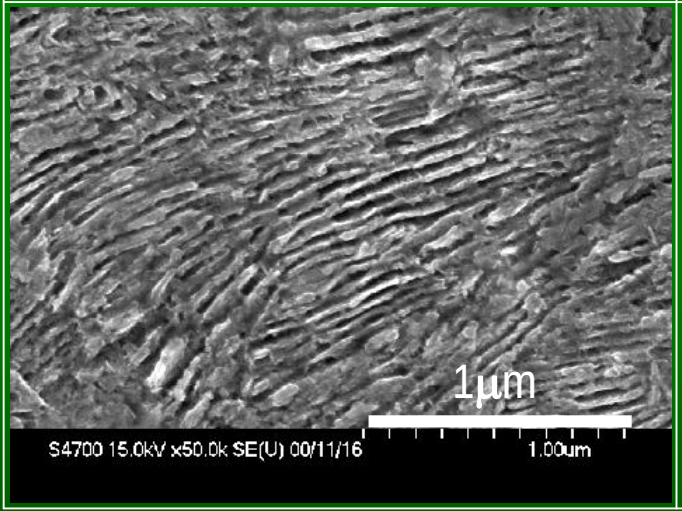
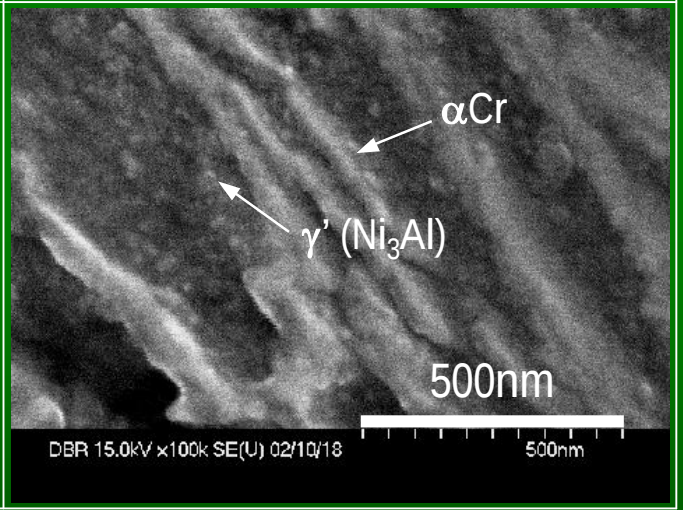
Charpy Impact Value



Microstructure after ST-AG

SEM images

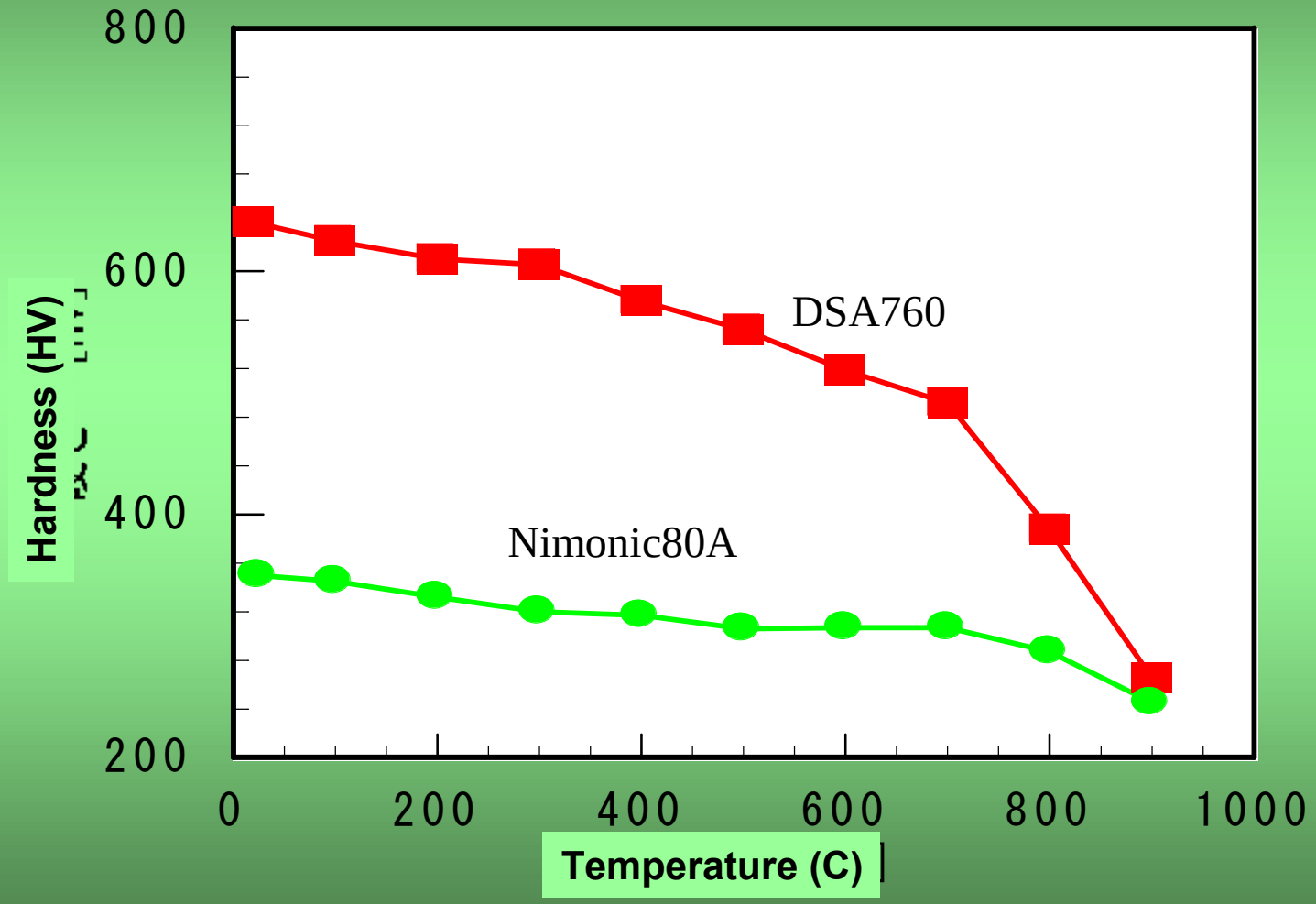
Solution treatment (ST) : 1150deg.C x over0.5hr / WC
Aging (AG) : 550deg.C x over16hr / AC

x50,000	x100,000
	

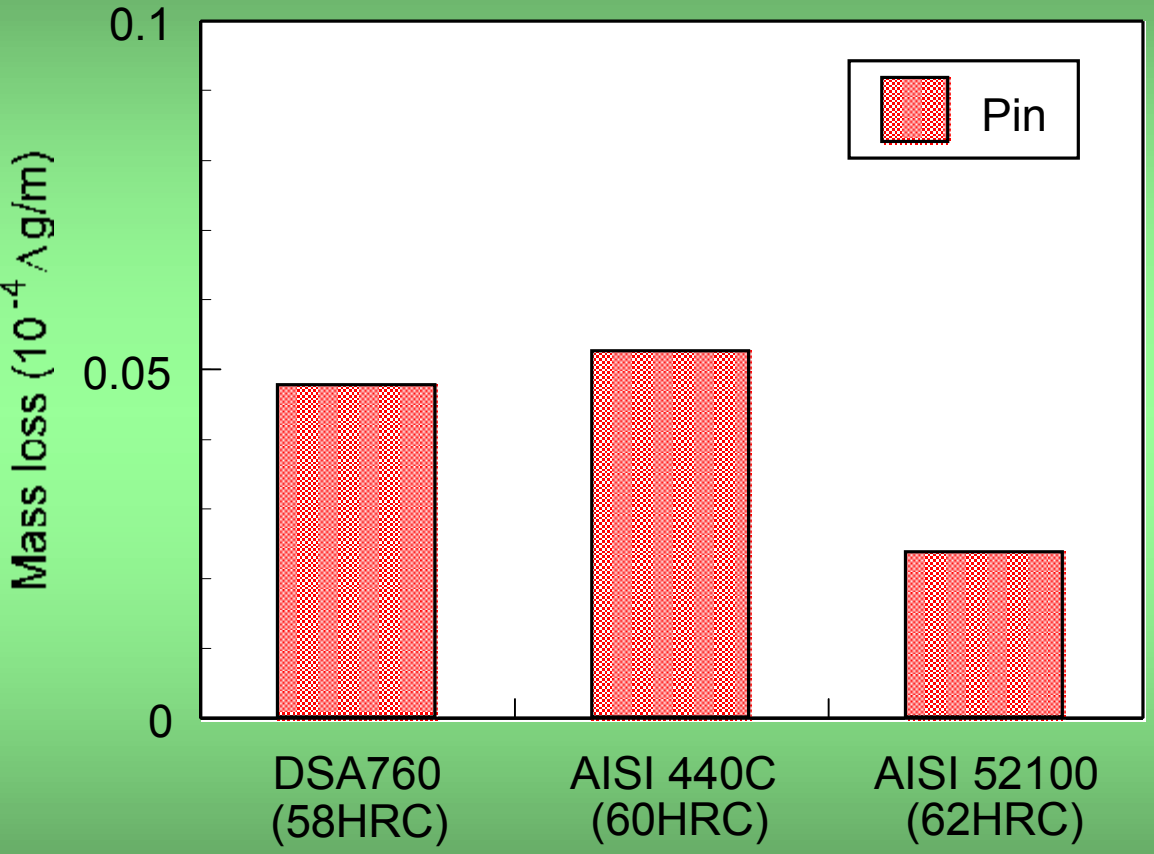
Hard phase consists of lamellar αCr and γ/γ' phases

γ' : Ni_3Al

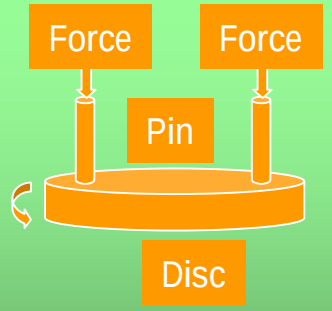
Hot Hardness



Wear Resistance

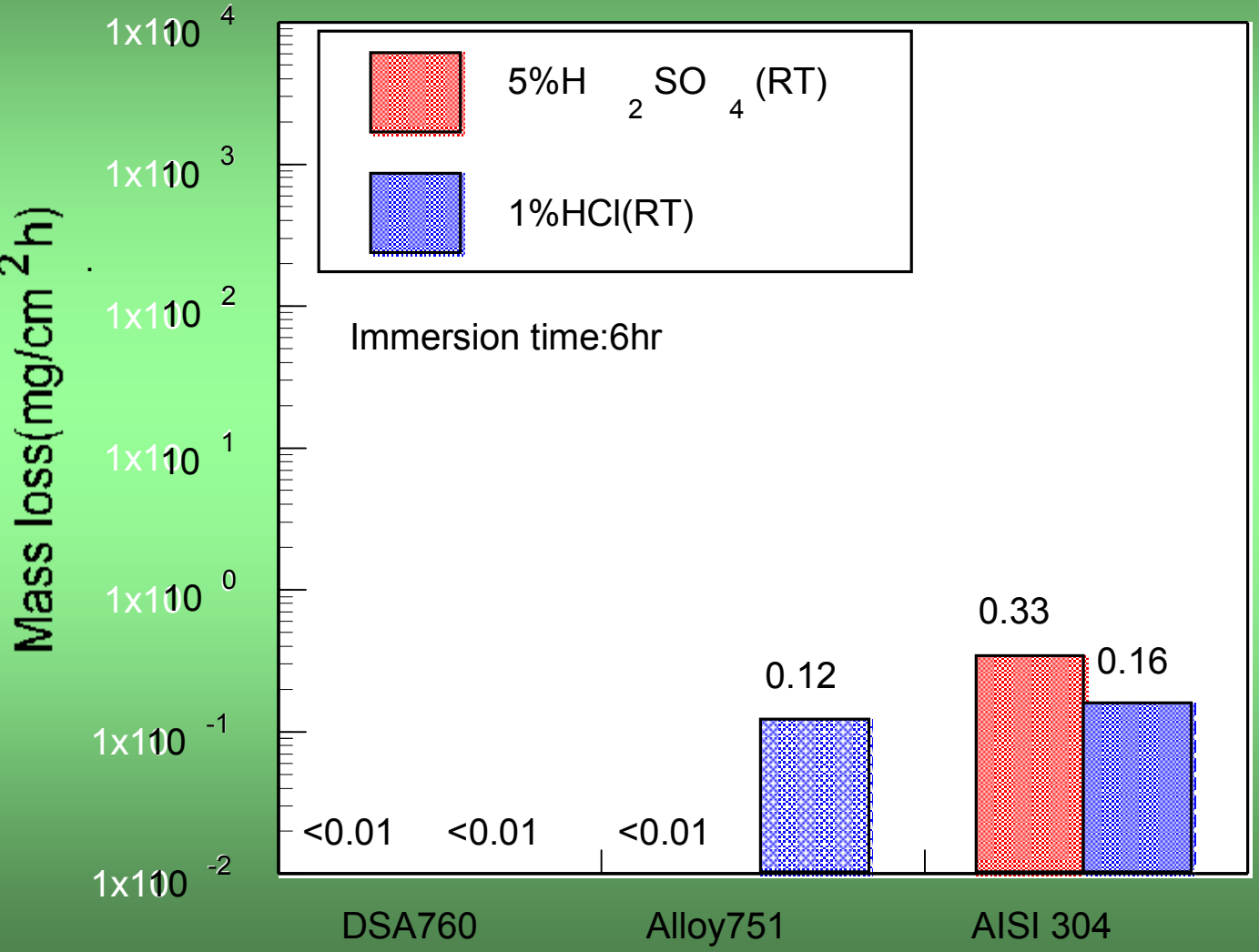


<Test condition>
Test temperature : RT
Contact force : 10kg
Distance : 10km
Rev. speed : 1m/s
Lubricant : dry
Partner disc : AISI 52100
(62HRC)



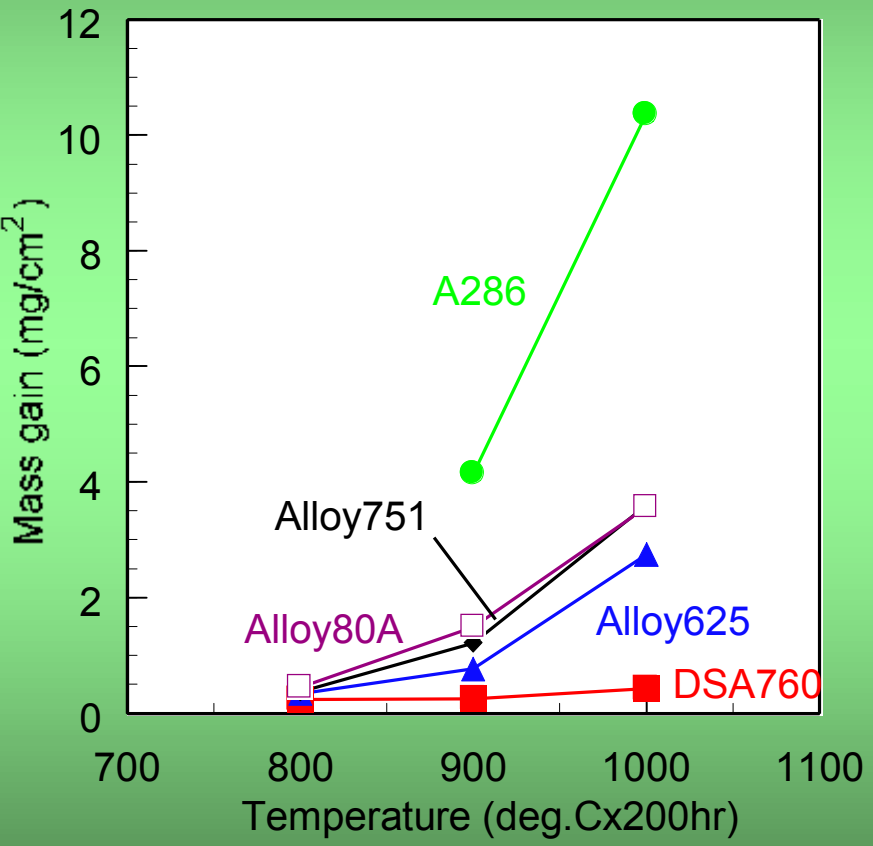
Pin-on-disc wear test

Acid Corrosion Resistance

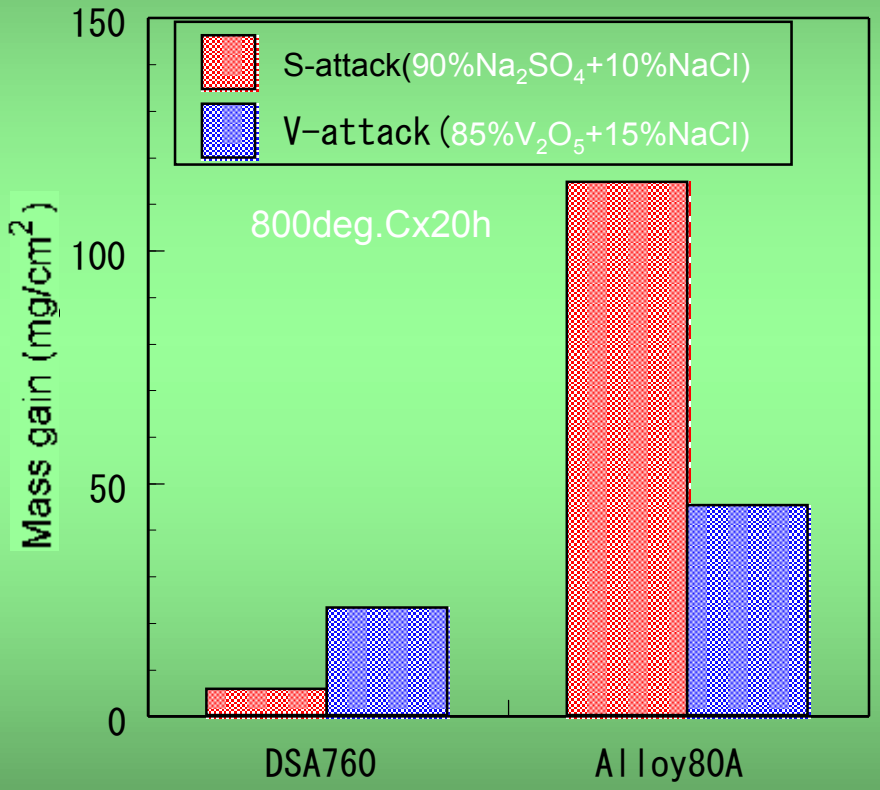


Hot Corrosion Resistance

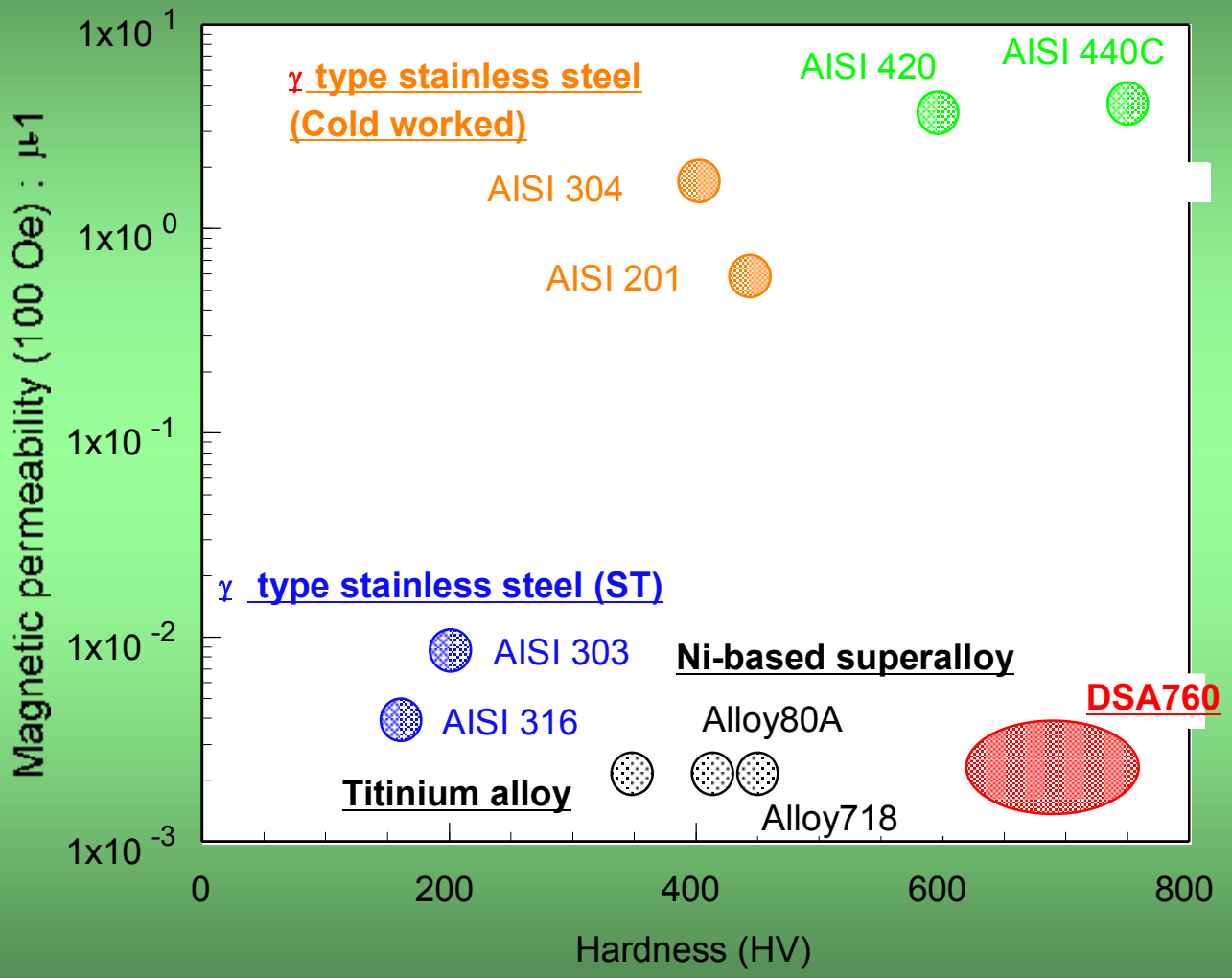
High temperature oxidation



Hot corrosion by salt coating



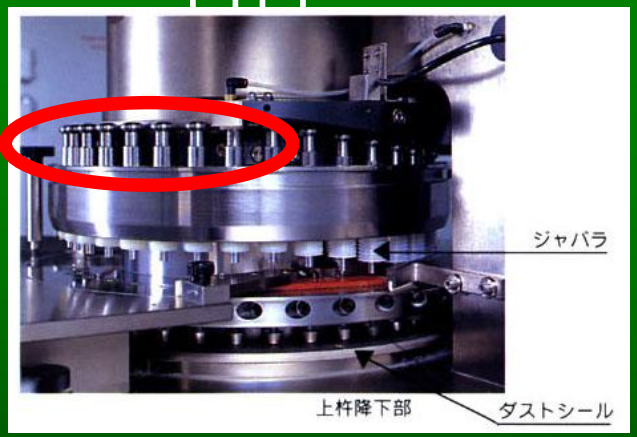
Hardness and Magnetic Permeability



Examples of Application (Tools)

- High hardness (High temperature)
- Excellent corrosion resistance

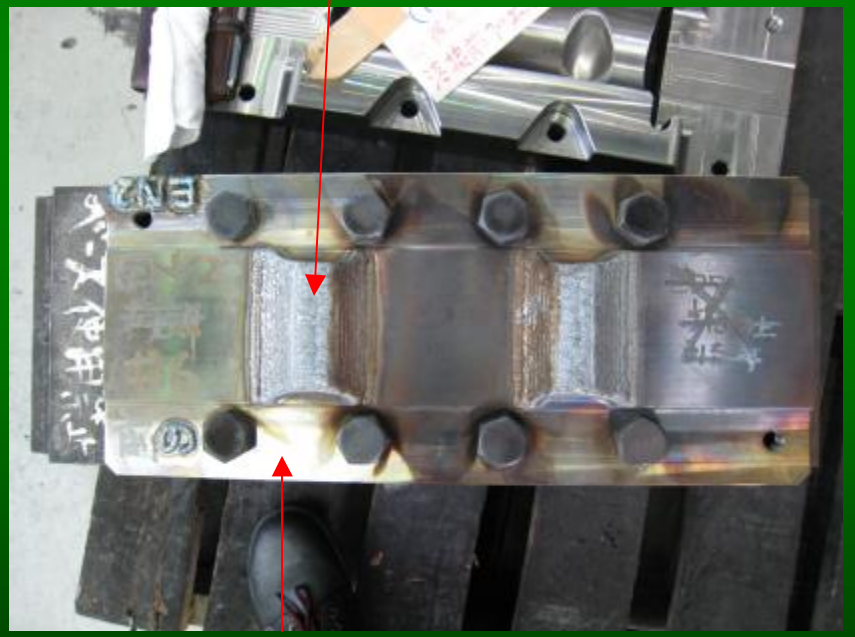
Die tool to make drug



Hot die punch

Weld Overlay by DSA760

Overlay:55HRC



Base:36HRC DAC3

Examples of Application (Wire, Bearings)

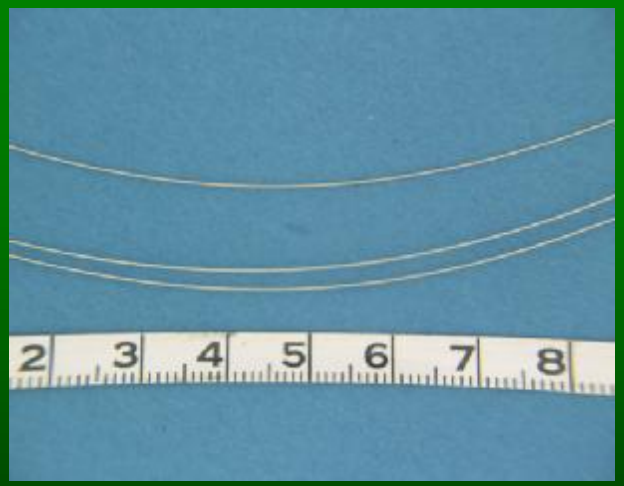
High Strength Wires

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？