

“Materials Korea – 소재강국 실현을 위한 프론티어”

Current Industrial Application and R&D Status on Titanium in Korea

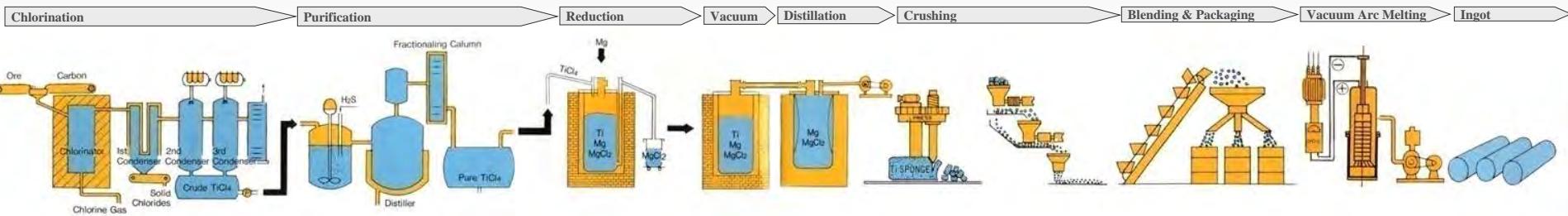
Dr. Yong Tai LEE

Director of Light Metals Division

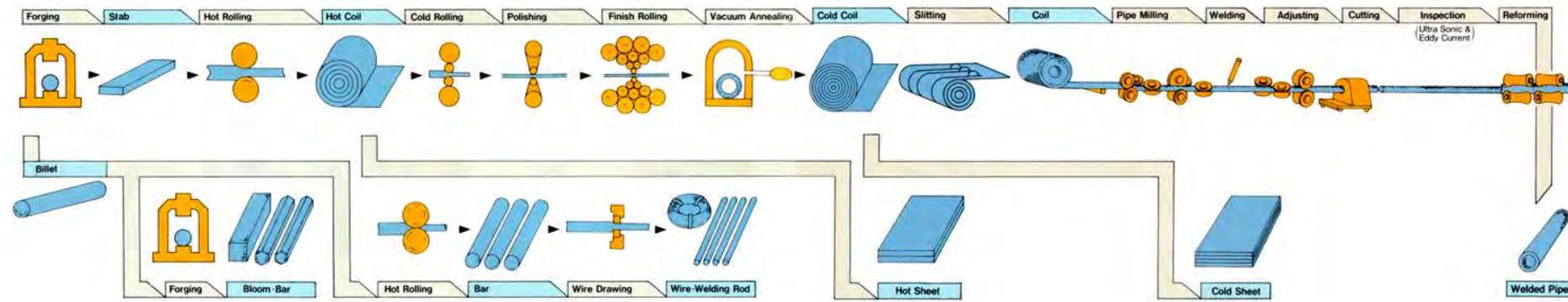
- ❖ Titanium Production & Consumption
- ❖ Titanium Import & Export in Korea
- ❖ Titanium Industrial Applications in Korea
- ❖ Titanium R&D in Korea

Titanium Production Flow

Titanium Sponge



Titanium Mill Product

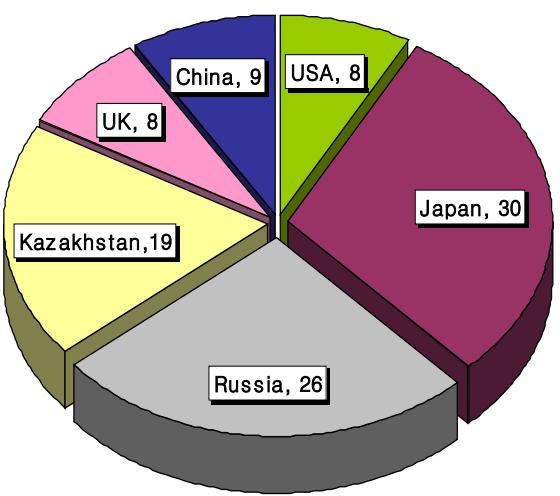


Titanium Production & Consumption in the World(2007) KIMS

SPONGE

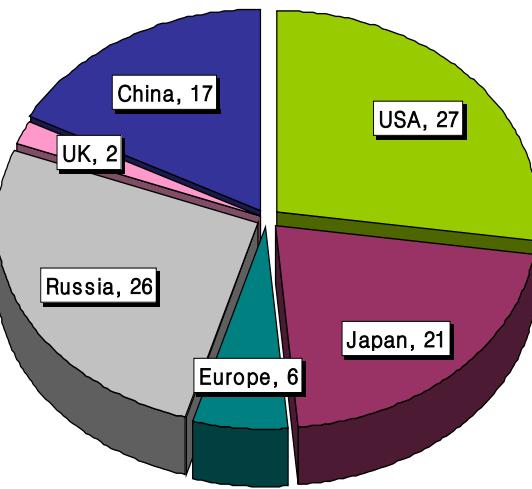
Production

	ton	%
USA	8,000	8
Japan	31,000	30
Europe	0	0
Russia	27,000	26
Kaza	19,000	19
UK	8,000	8
China	9,500	9
Total	102,500	100



Consumption

	ton	%
USA	28,000	27
Japan	22,000	21
Europe	6,500	6
Russia	27,000	26
UK	2,000	2
China	17,000	17
Total	102,500	100

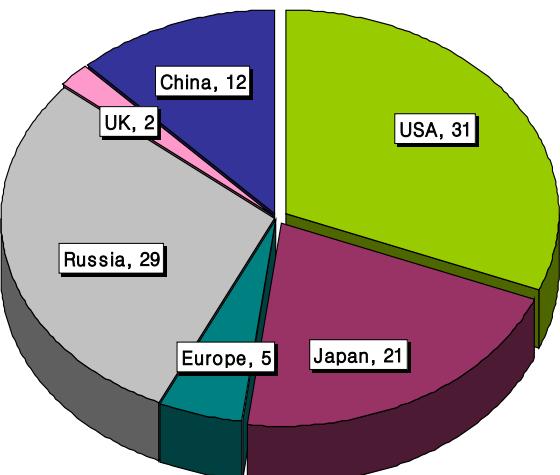


Production

	ton	%
USA	26,300	31
Japan	18,000	21
Europe	4,500	5
Russia	24,000	29
UK	1,900	2
China	9,300	12
Total	84,000	100

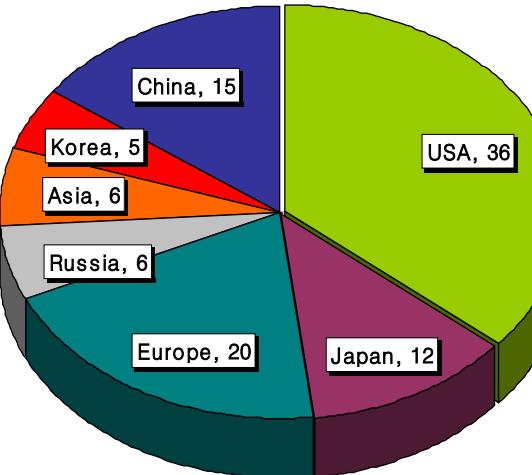
Mill Products

Production



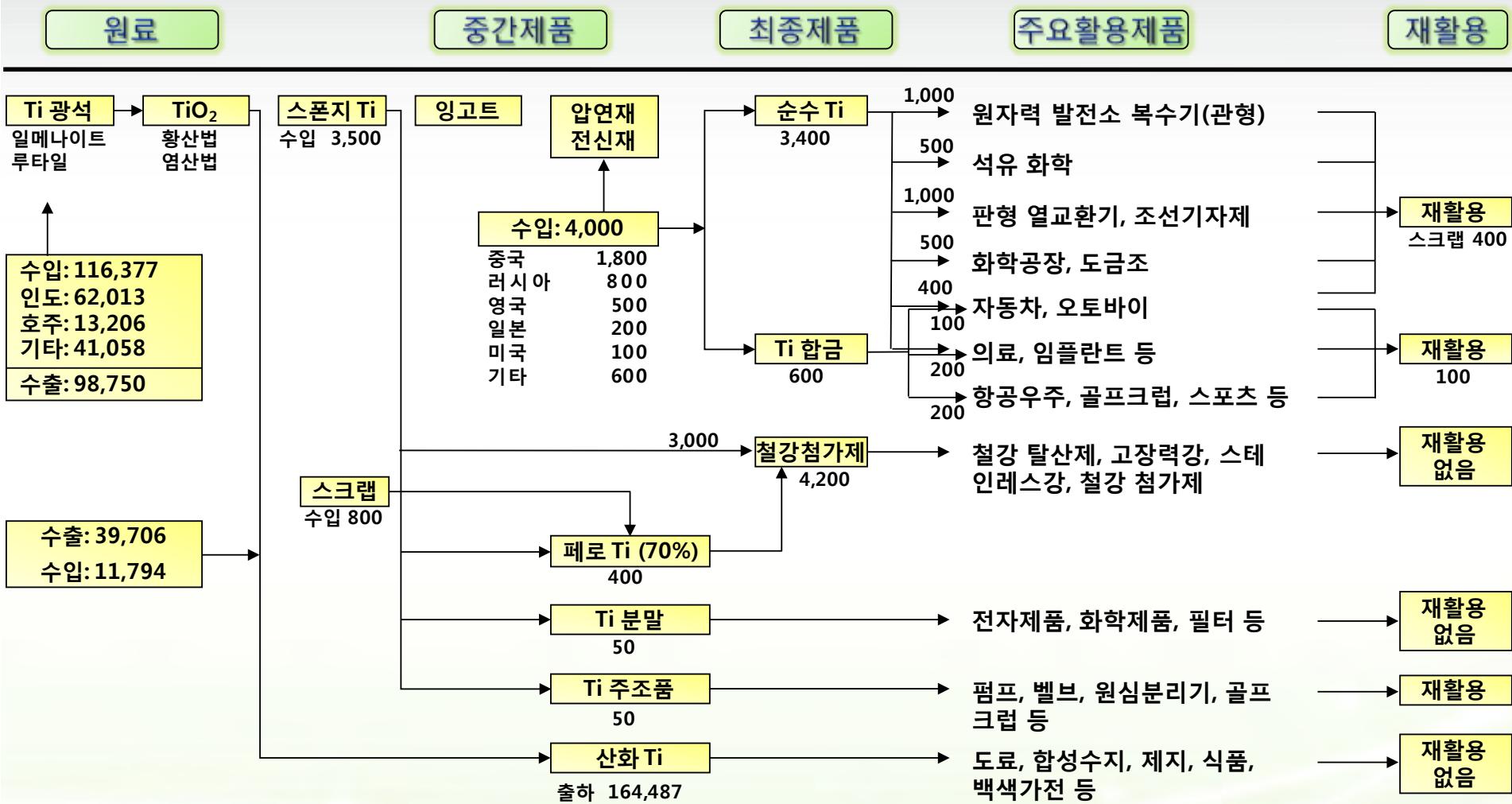
Consumption

	ton	%
USA	30,000	36
Japan	10,000	12
Europe	17,000	20
Russia	5,000	6
Asia	5,000	6
Korea	4,000	5
China	13,000	15
Total	84,000	100



Source : Fundamentals of Titanium and Its Works (2008)

Titanium Flow in Korea (2009)

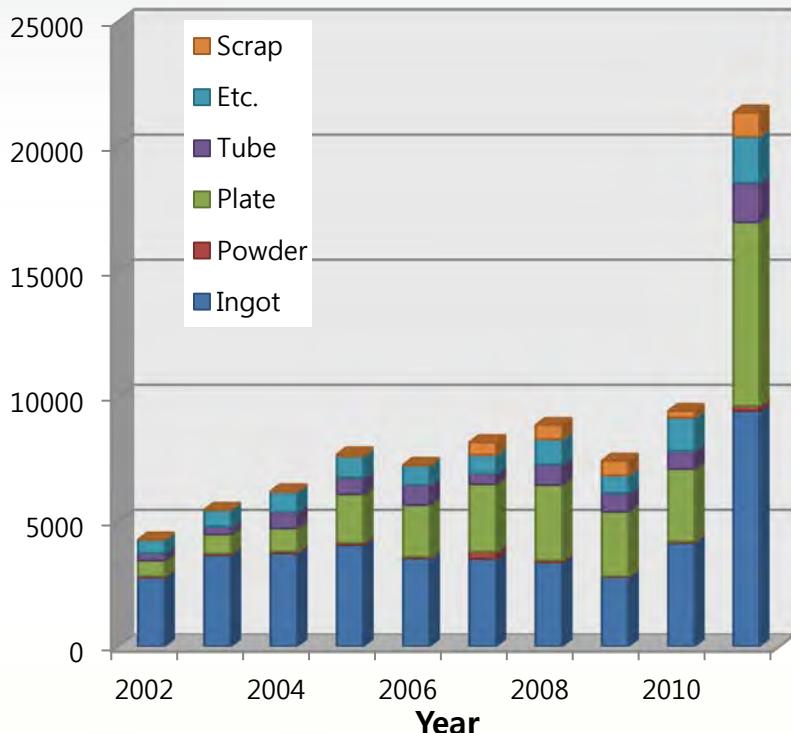


출처 : 한국무역통계 (2007) 및 추정자료 (이용태)

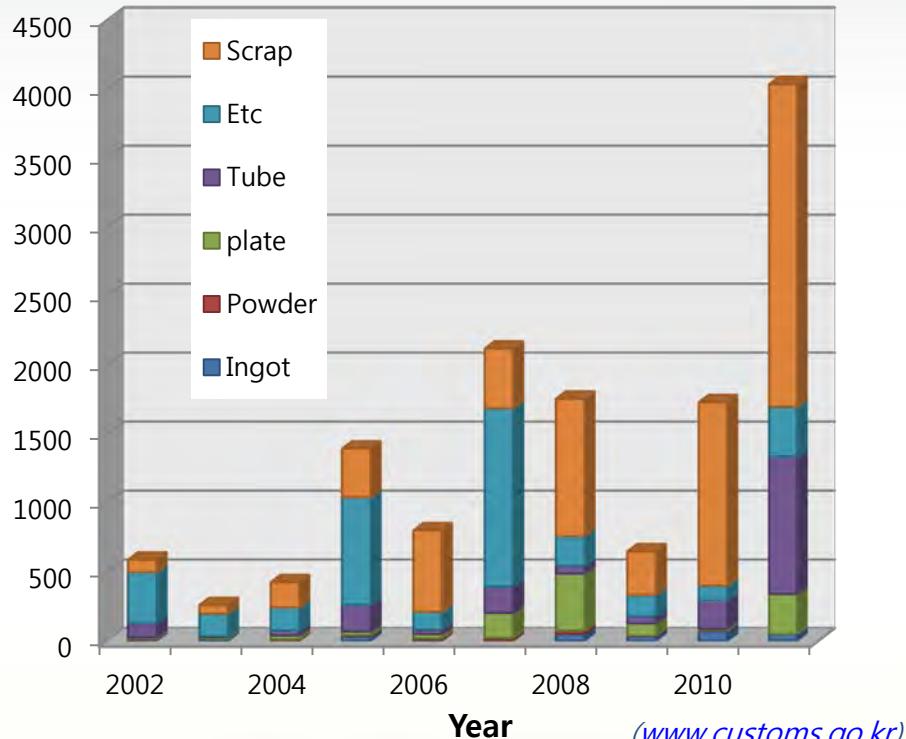
Export and import of Titanium in Korea

KIMS

❖ Imports of Ti products (ton), 2002 to 2011



❖ Exports of Ti products(ton), 2002 to 2011



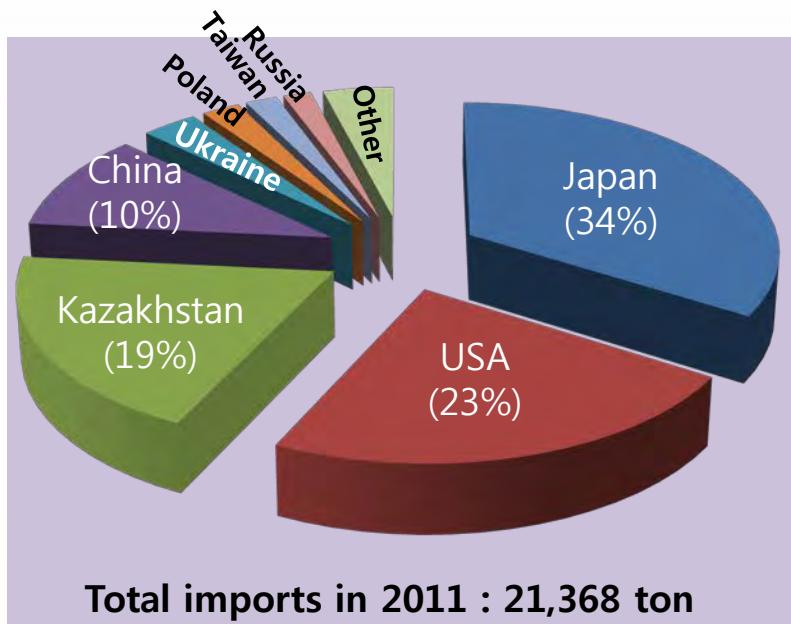
(www.customs.go.kr)

- ▷ Domestic Ti consumption relies mostly on overseas supply.
- ▷ Ti consumption has increased steadily over the last 10 years. Imports of Ti products peaked at 21.3kt in 2011.
- ▷ Exports of Ti in Korea are mainly scrap and secondary processing articles (tube, plate etc.). They are also increasing and reached 4kt in 2011.

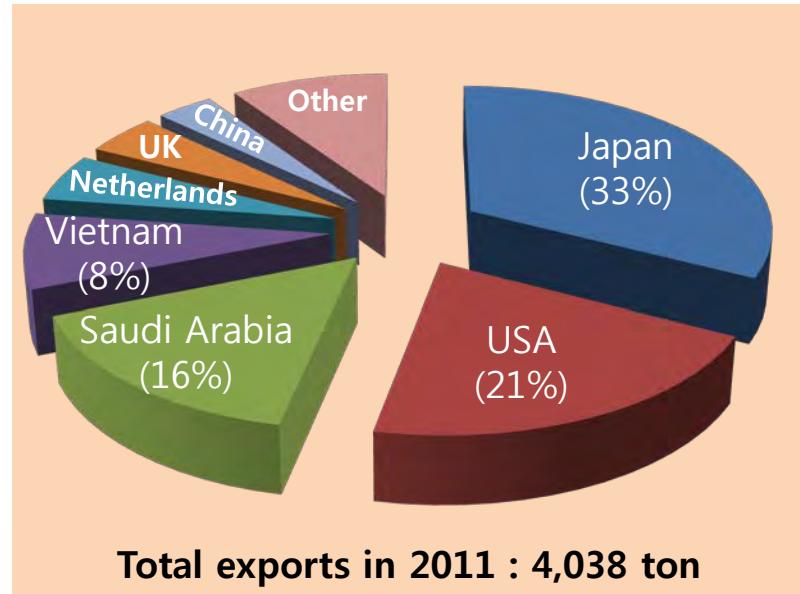
Import and Export of Titanium to the World

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Imports in 2011



Exports in 2011

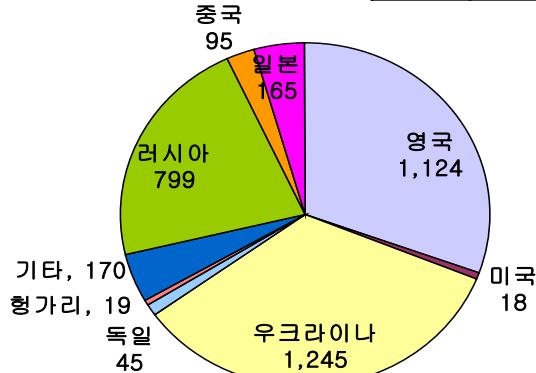


- ▷ Korea is an important market for Ti with imports of sponge and mill products coming mainly from Kazakhstan, the UK, Ukraine, Russia, Japan, USA and China.
- ▷ Imports of unwrought Ti and mill products were 21.4kt in 2011.
- ▷ Imports of Ti mill products and articles came mainly from Japan, Poland and the USA.

Titanium Import Countries in Korea

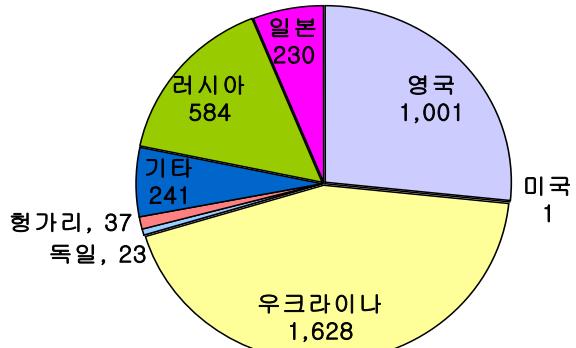
2003

I	3,680
E	16



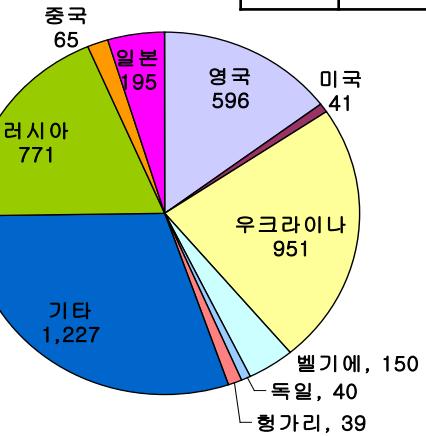
2004

I	3,745
E	2



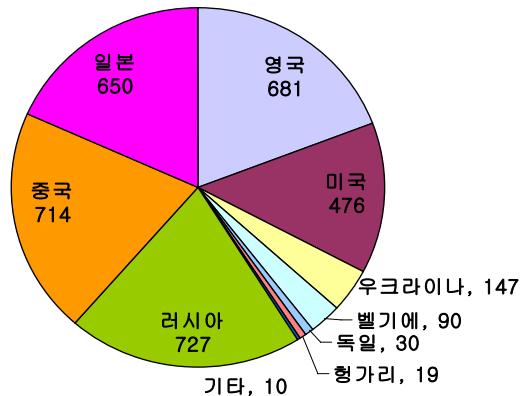
2005

I	4,075
E	34



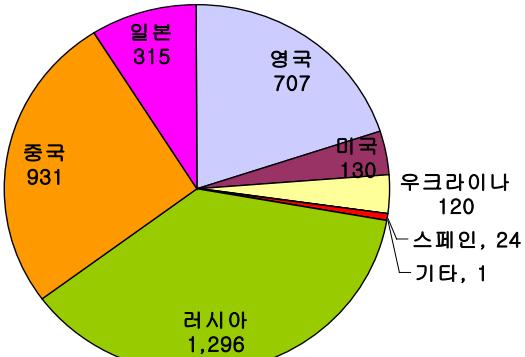
2006

I	3,544
E	6



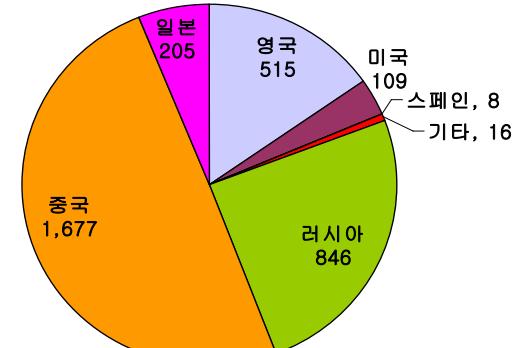
2007

I	3,524
E	2



2008

I	3,376
E	52



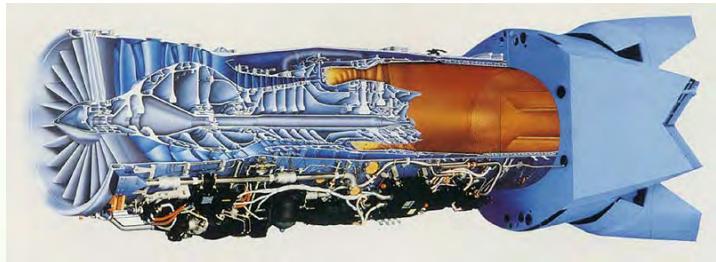
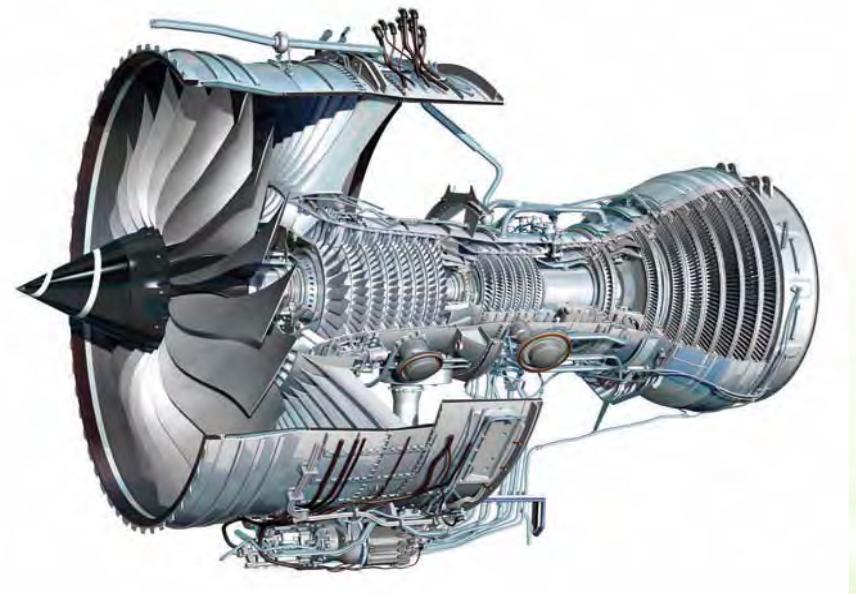
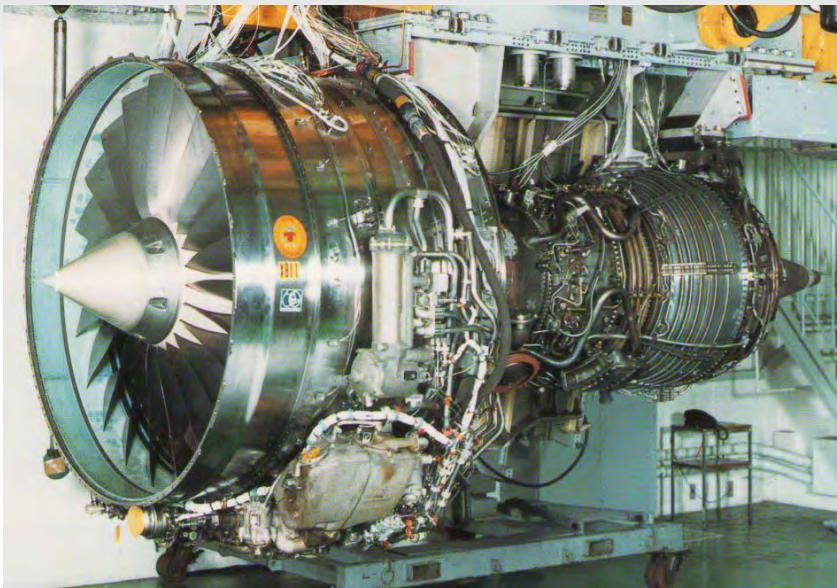
Titanium Rod & Wire Imports for Medical Purpose **KIMS**

Source: Korea Customs Service, Unit: ton

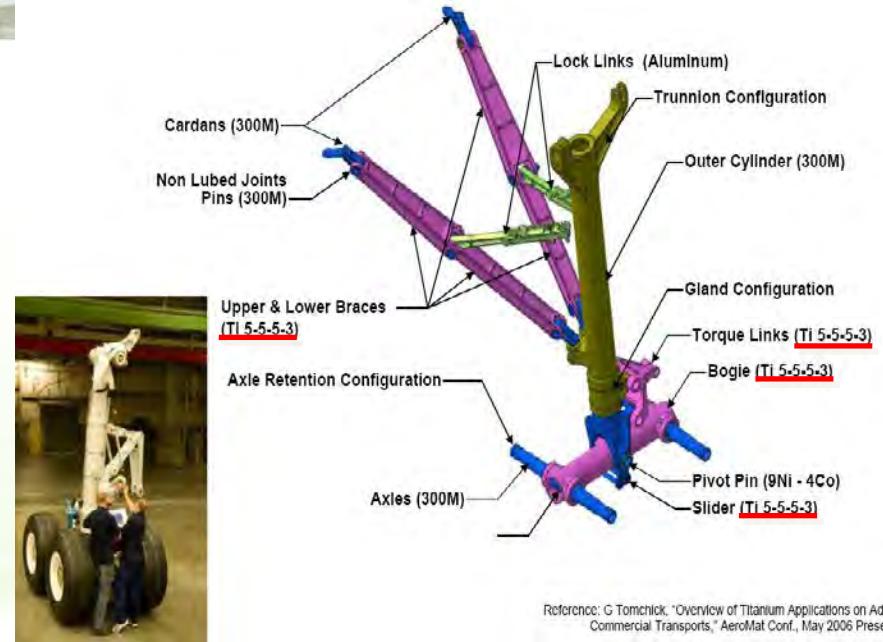
Year	2005	2006	2007	2008	2009	2010	2011	2012(1-4)
USA	344	259	277	515	270	876	1,010	366
Japan	448	380	229	261	248	188	457	62
China	23	40	49	78	66	123	242	93
Germany	3	9	11	5	3	37	15	6
England	-	4	17	5	4	10	12	2
Taiwan	-	2	10	14	9	12	16	3
France	12	33	52	53	45	64	43	6
Italy	13	-	74	55	21	-	14	1
Liechtenstein	-	-	-	1	1	1	1	-
Israel	-	-	-	-	-	-	1	-
Norway	-	-	-	-	1	-	16	-
Swiss	1	1	1	-	-	-	-	-
Netherland	-	21	-	-	-	-	-	-
Poland	-	18	1	-	-	-	-	-
Australia	-	-	-	-	-	-	1	-
Hong Kong	-	-	-	-	-	-	1	-
Sweden	-	-	-	-	-	1	1	-
Russia	16	9	15	10	15	14	20	-
Singapore	-	-	-	1	3	-	1	-
Total	852	776	737	998	686	1,328	1,851	541

Aerospace (1)

KIMS



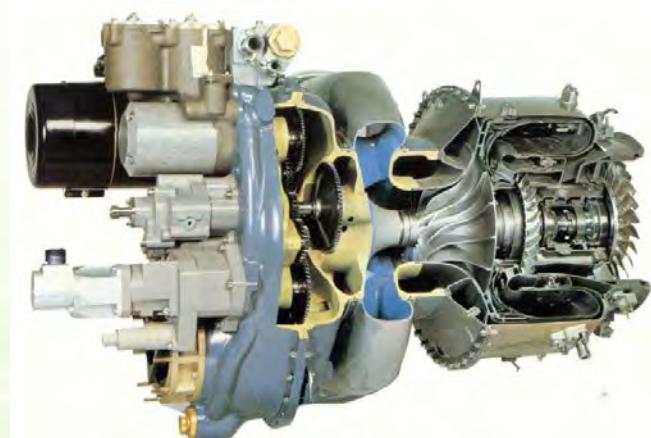
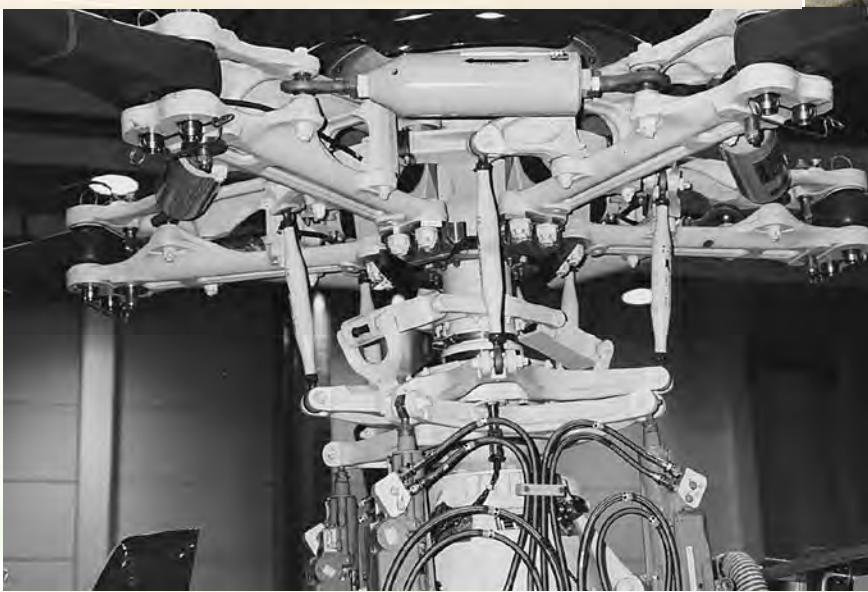
Aerospace (2)



Reference: G Tomchick, "Overview of Titanium Applications on Advanced Commercial Transports," AeroMat Conf., May 2006 Presentation

Aerospace (3)

KIMS



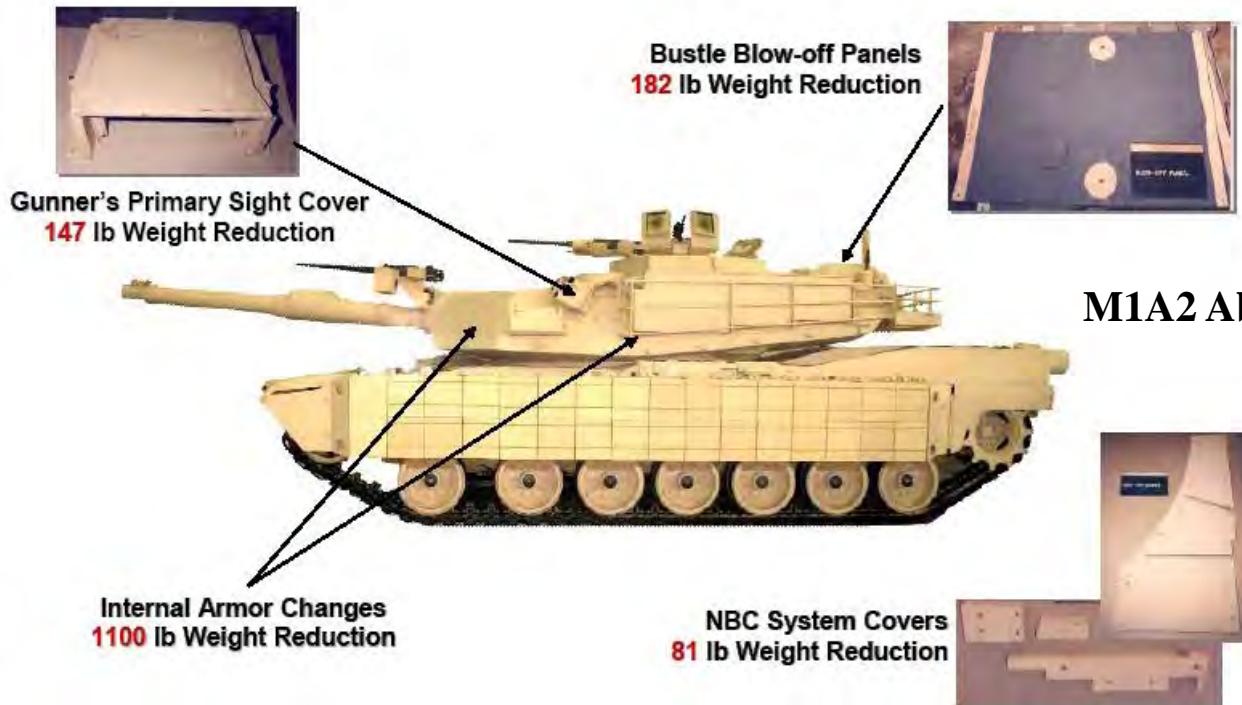
Aerospace (4)

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Militaries (1)

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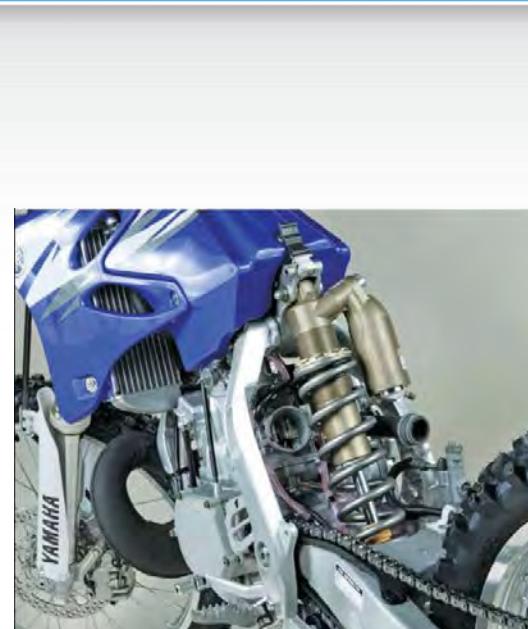
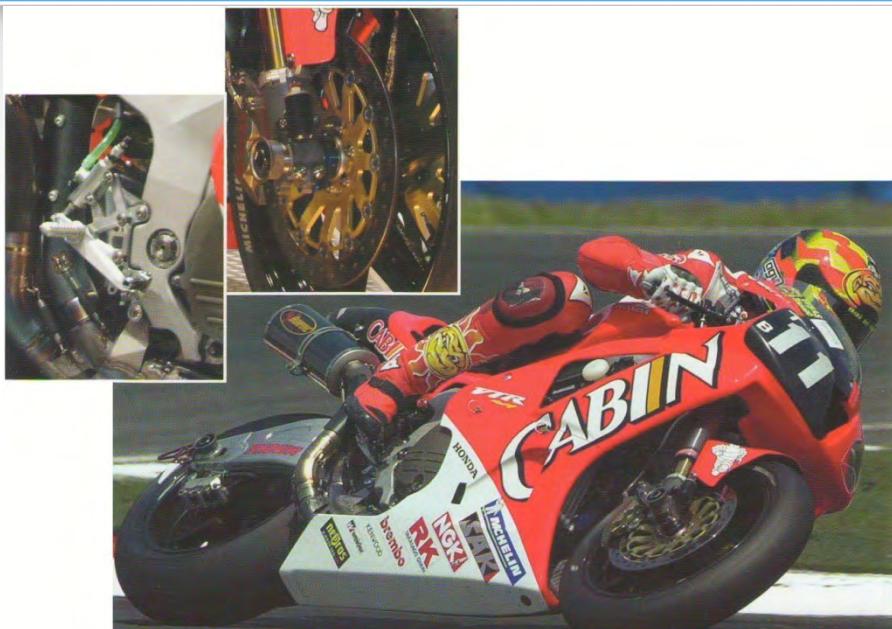
Militaries (2)

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Automobiles (1)

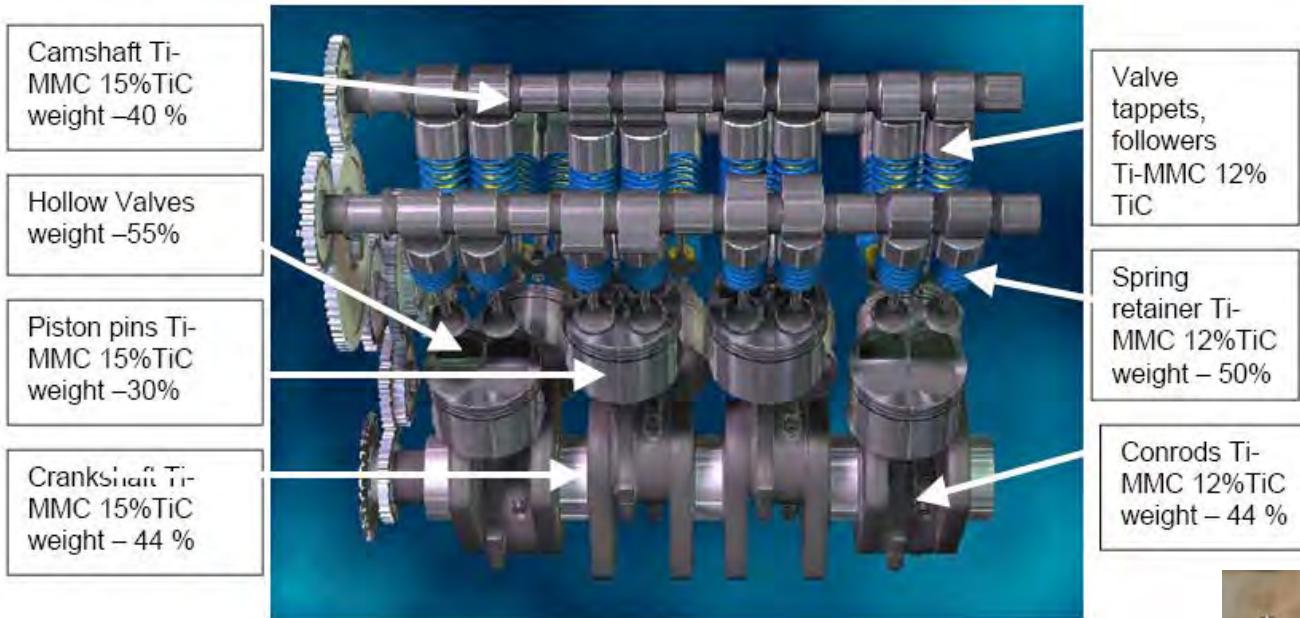
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aei material innovations

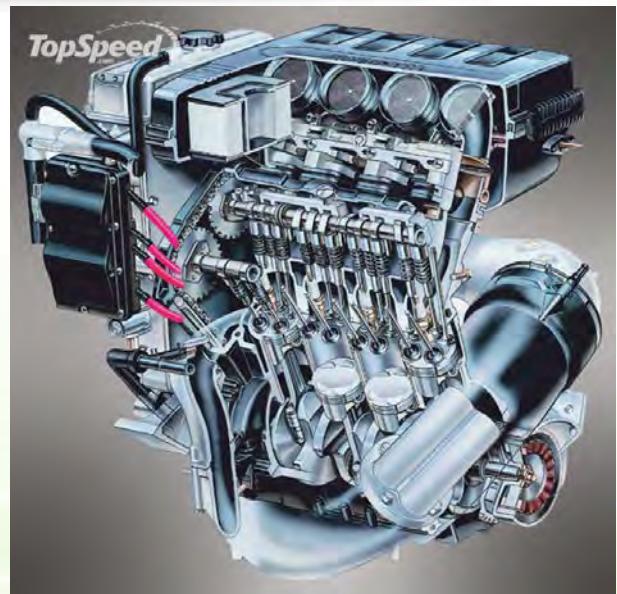


Automobiles (2)



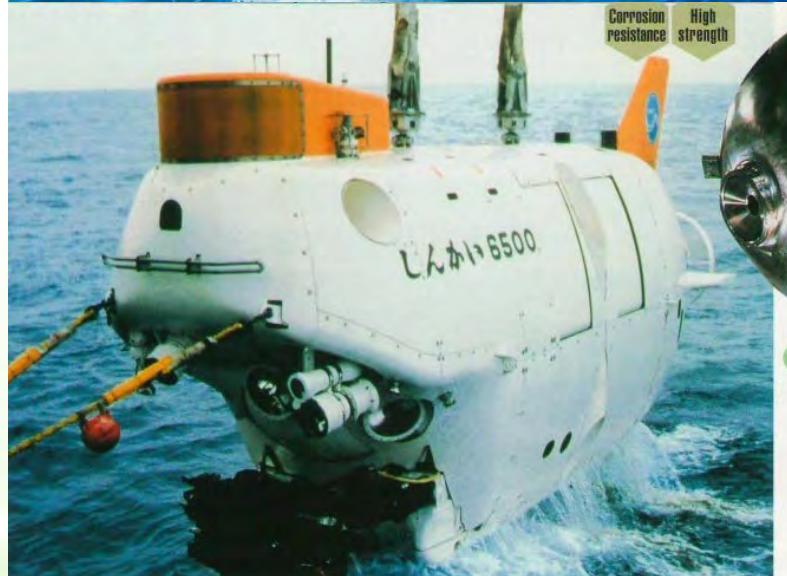
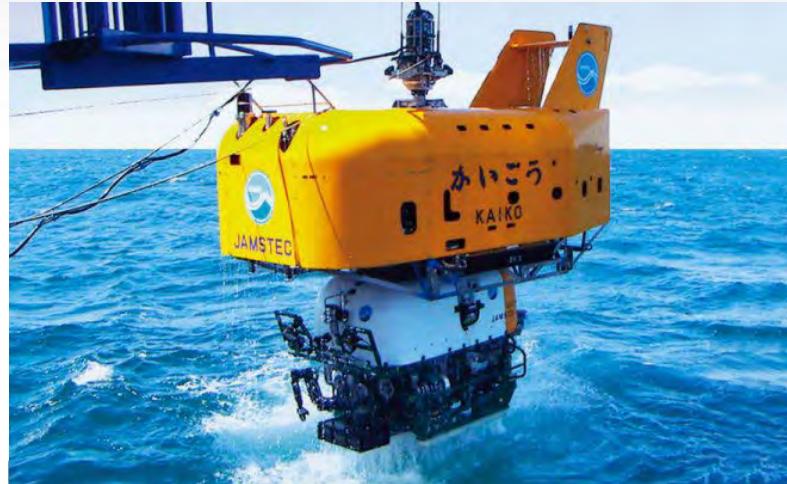
Automobiles (3)

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Off-shores

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Desalination (MSF Single Module Evaporator Transportation)



MSF Evaporator of Umm Al Nar Desalination Plant Station 'B' (UAE, 12.5 MIGD x 5 Units, W x H x L = 20 x 5 x 100 m)

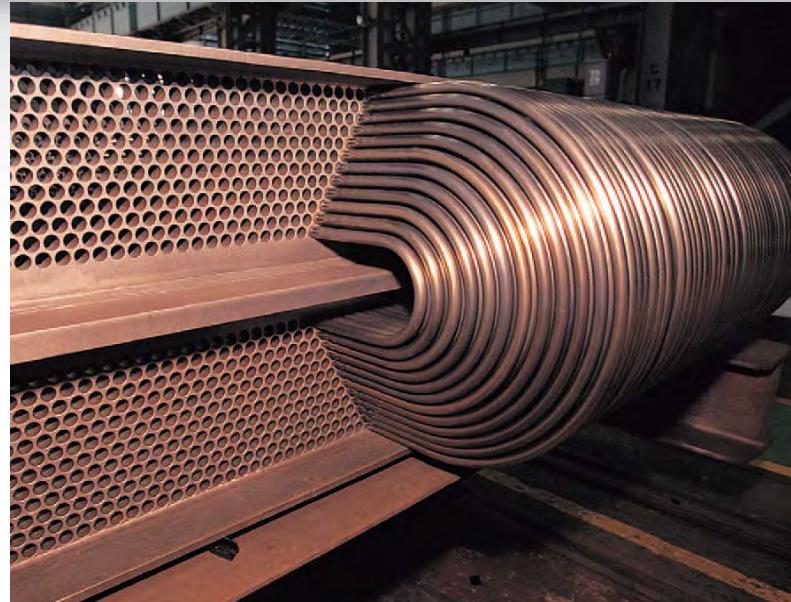
Desalination (Benghazi North CCPP MED Plant) KIMS



Benghazi North CCPP MED Plant (Libya, 0.55 MIGD x 2 Units)

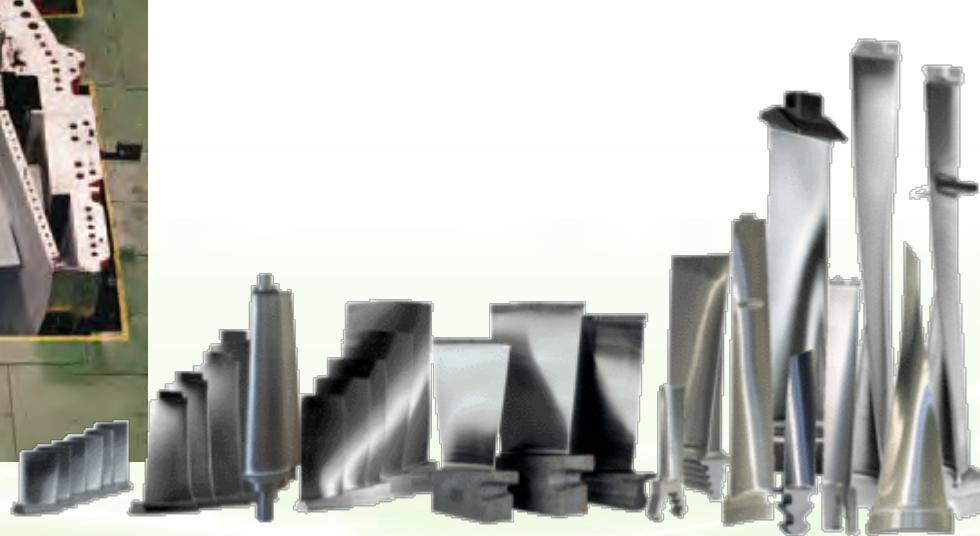
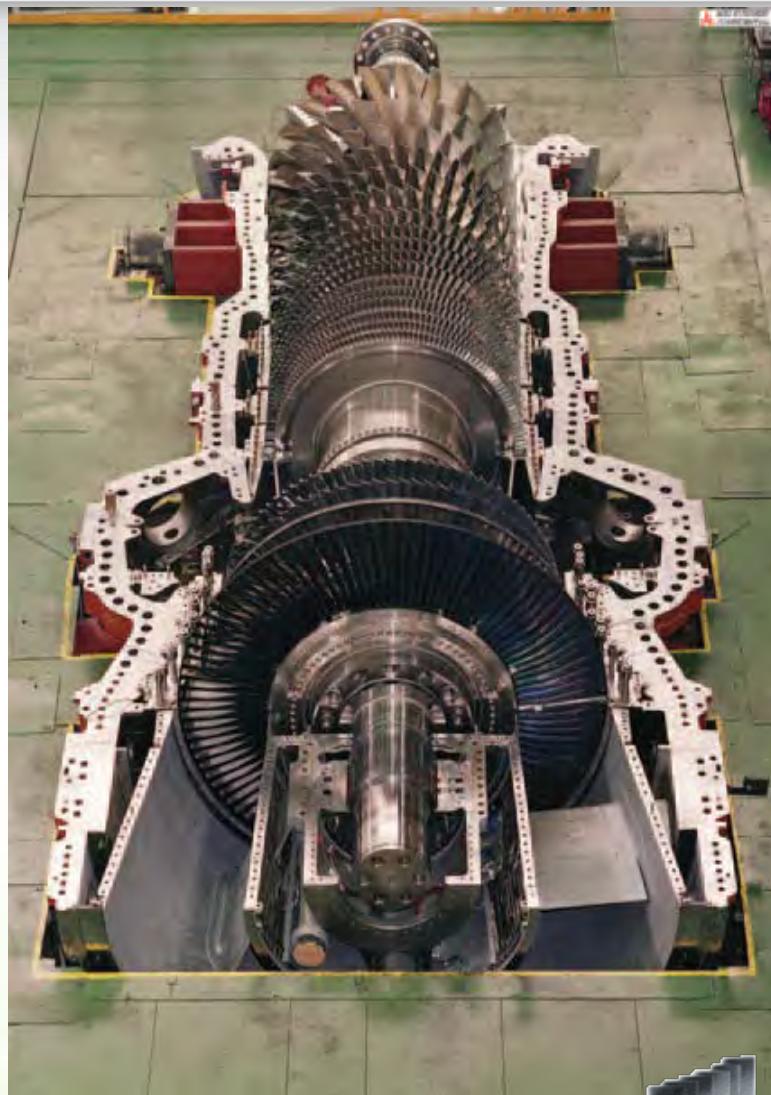
Desalination

KIMS



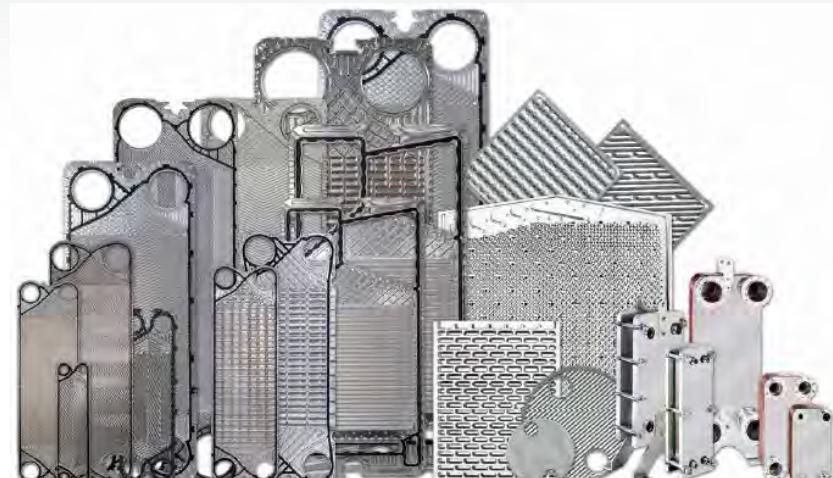
Power Generations (1)

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Power Generations (2)

KIMS



Chemicals

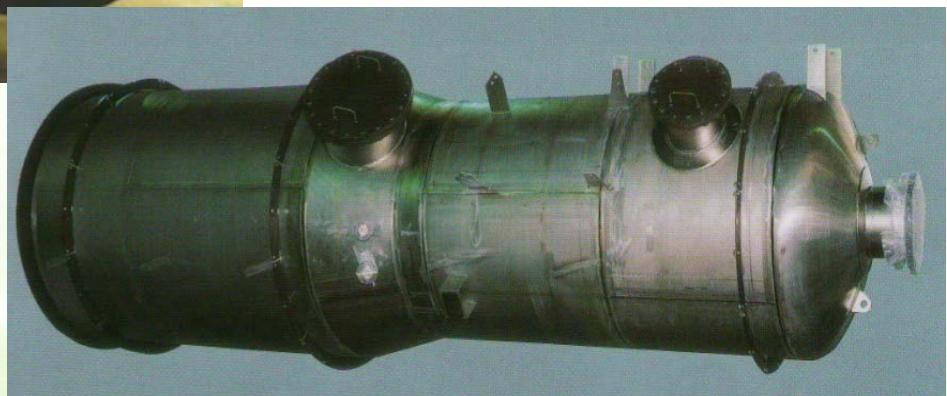
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Titanium piping for chemical plants

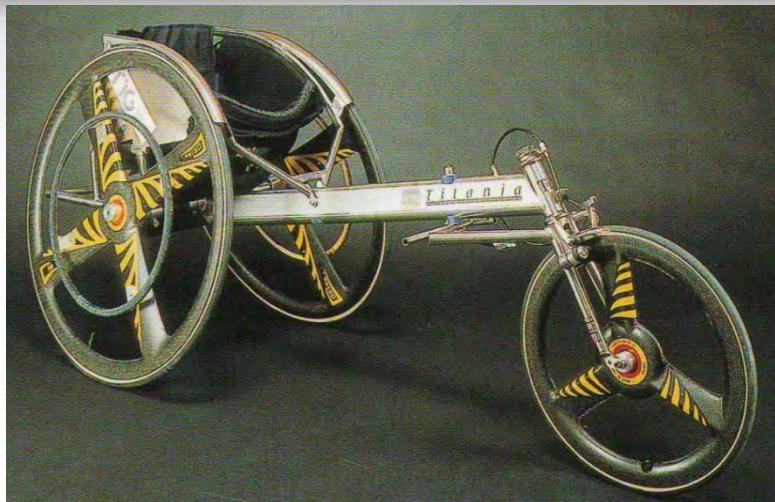


Titanium reaction tank



Sports & Leisure (1)

KIMS



Sports & Leisure (2)

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Commodities

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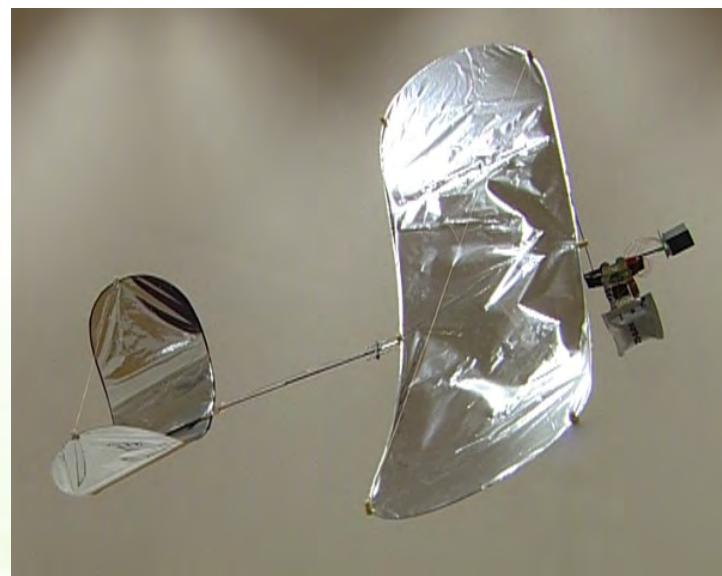
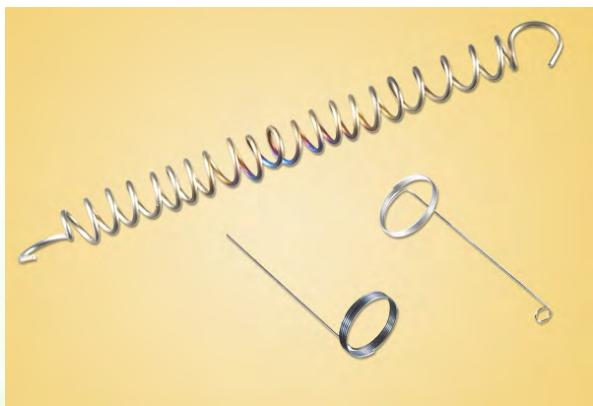
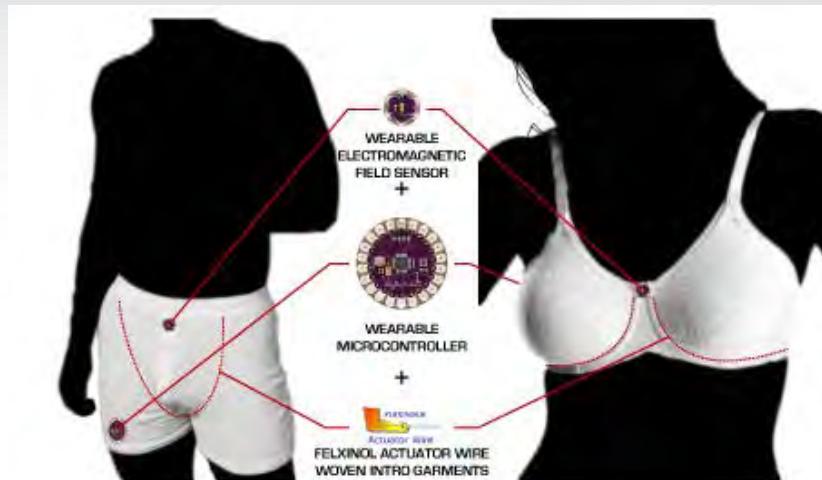


pcBee
대한민국 PC정보



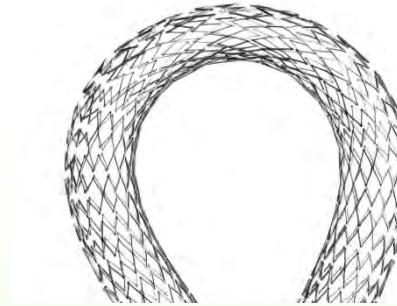
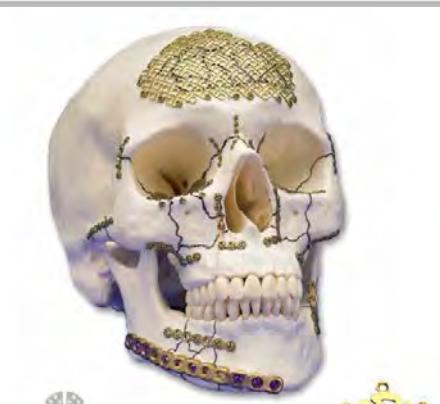
Functional Applications

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Biomedicals

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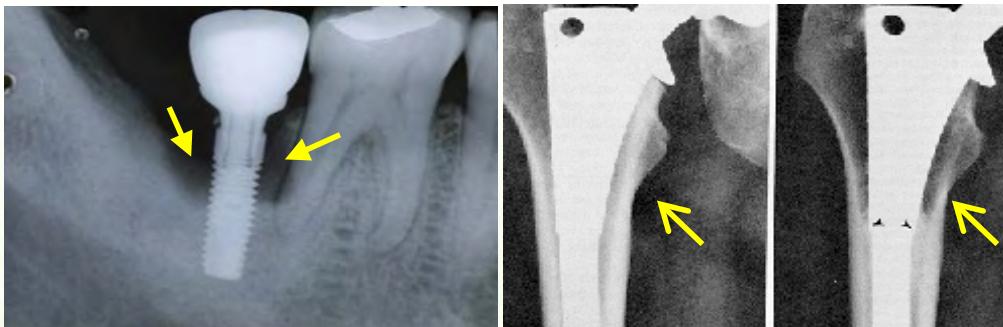
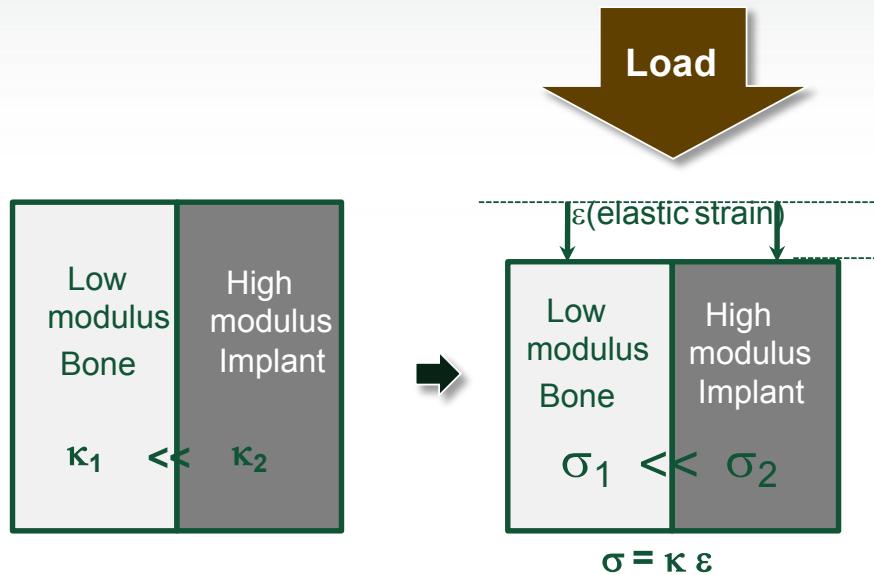
R&D and Production History of Titanium in Korea

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		In the 1980s	1995	2000	2005	2010
Research Institute	KIGRAM	Refining	Ti melting			High purification
	KIST		Ti melting			Ti cladding
	KIMM(KIMS)		Characterisation	Ti melting/casting	Alloy development	
	RIST		Ti rolling	Welding		Ti refining
	ADD			Military application of Ti parts		
	KITECH				Bio-application	
University	POSTECH		Physical metallurgy	Forming processing		
	SKKU		Ti casting	Mold development	Oxidation	
	KAIST			Ti intermetallics	Phase transformation	
	Kangnung Univ.			Phase transformation	Beta Ti alloy	
	GSNU			Ti-Ni shape memory alloy		
	Inha Univ.				Severe deformation	
	CNU					Bio application
	CBNU					Surface treatment
Industry	KOSMO Chem.	Korea Titanium('72)	Ilmenite/rutile		KOSMO chem.	
	POONGSAN		Condenser tube for power plant			
	HYUNDAI Titanium		Sales of Ti products	Heat exchanger tube	Weldings	
	SEAH			Titanium pipe		
	KOS LIMITED			Titanium wire		
	KPC			Ti melting/casting	Titanium valve	
	TSM Tech			Ti pressure vessel	Titanium cladding	
	OSSTEM				Titanium implant	
	ALL Met				Titanium weldings	
	NIB				Ti melting/casting	
	TAEWOOONG				Ti ring forging	
	MEC				Fe-Ti	

Why Titanium? – Stress Shield Effect

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Cortical bone : 10~30GPa
Ti alloys : 100~110GPa
Co alloys : 200GPa
STS316L : 205GPa

Elastic Modulus Difference between Bone/Implant

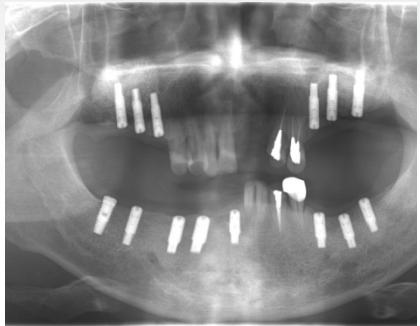
Stress Shielding Effect

Bone In-growth failure
Cortical bone loss; osseointegration

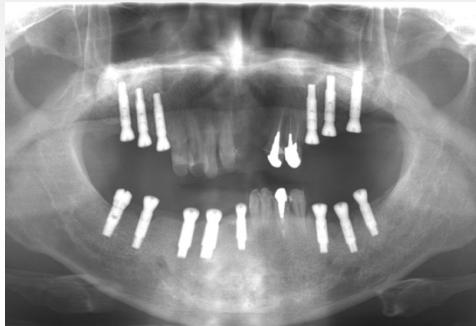
Implant failure/re-operation

Development of low modulus alloys

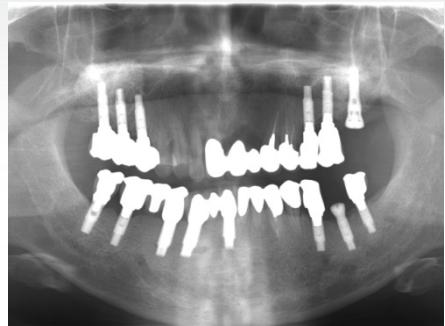
Failure Analysis of Implant



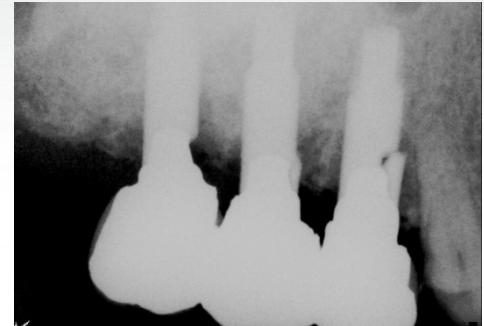
2006.09.26



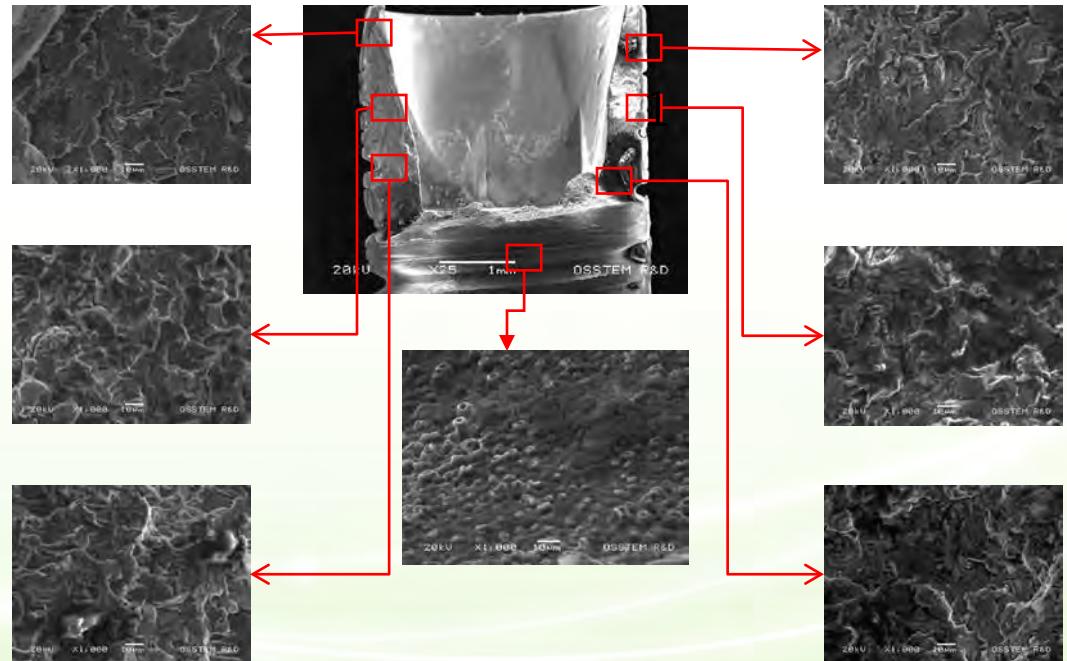
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2008.03.28

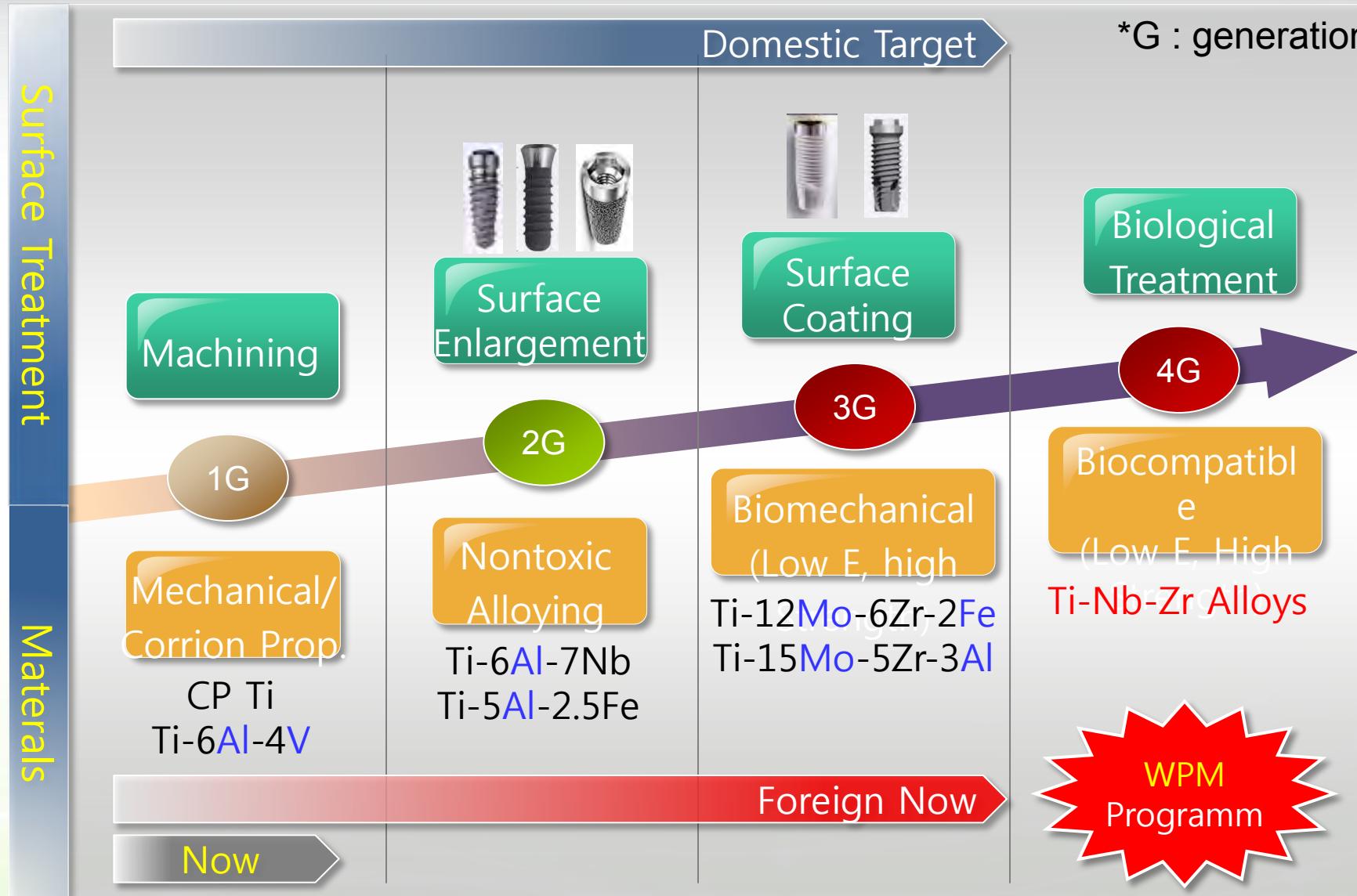


2010.04.20

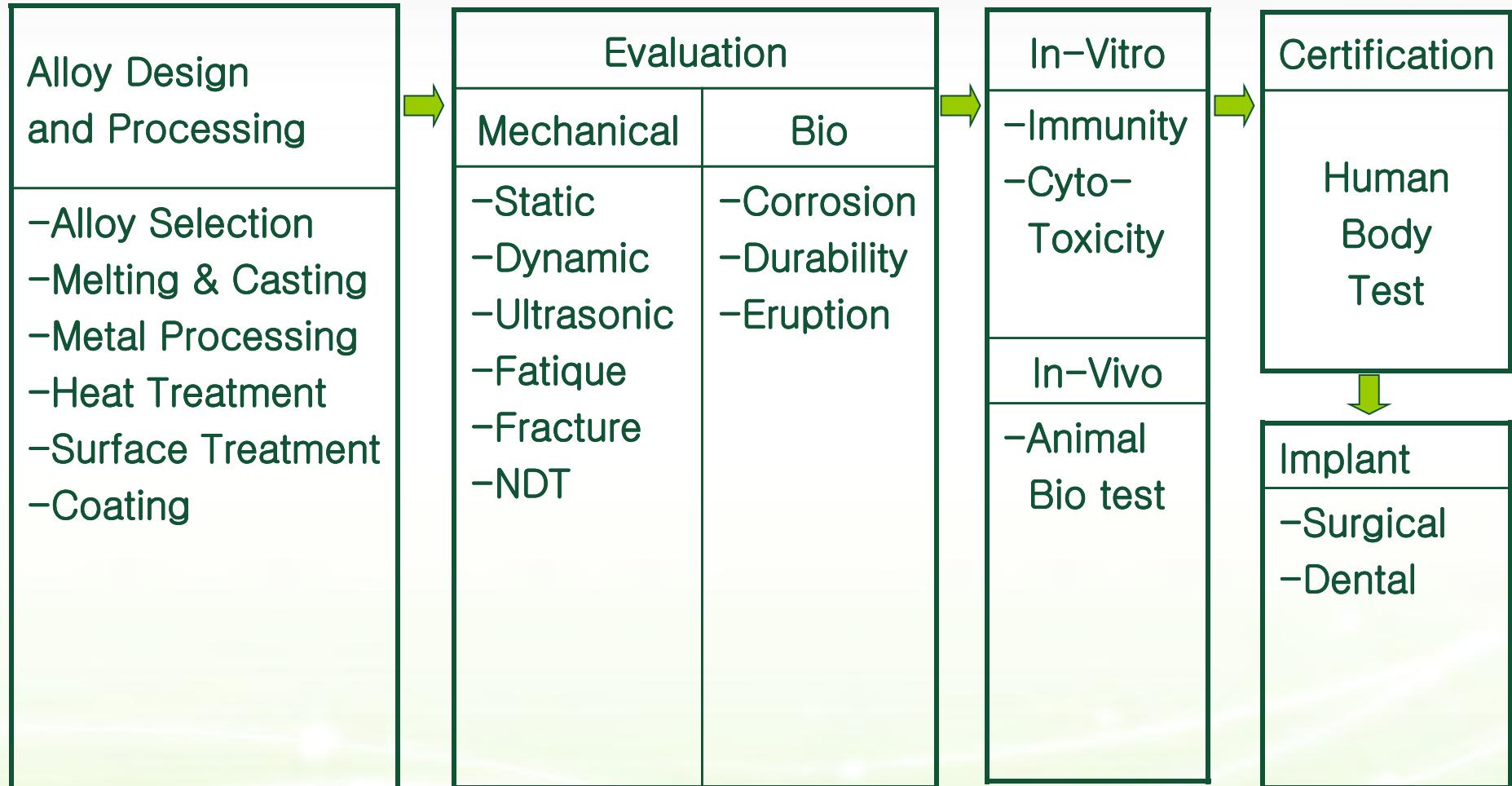


Development of Titanium Implants

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Development of a Biomaterial Parts



DV-X α Cluster Method

This approach is based on the theory of molecule orbital by electron circulation.

- electrons move atomic orbitals
- LCAO (Linear combination of atomic orbitals) method

아다치 히로히코(足立裕彦)

모리나가 마사히코(森永正彦)

나스 센자부로(那須三郎),
(1973)

Wave function is related to potential of atomic orbital

$$\psi_i = \sum_j C_{ij} \chi_i(l)$$

While molecular orbital function is expressed by

$$\sum_j (H_{ij} - \varepsilon_k S_{ij}) C_{jk} = 0$$

This function is transformed by Hamiltonian equation into the followed matrix

$$H_{ij} = \int \chi_i^*(l) H \chi_j(l) dv_1$$

H: electron Hamiltonian

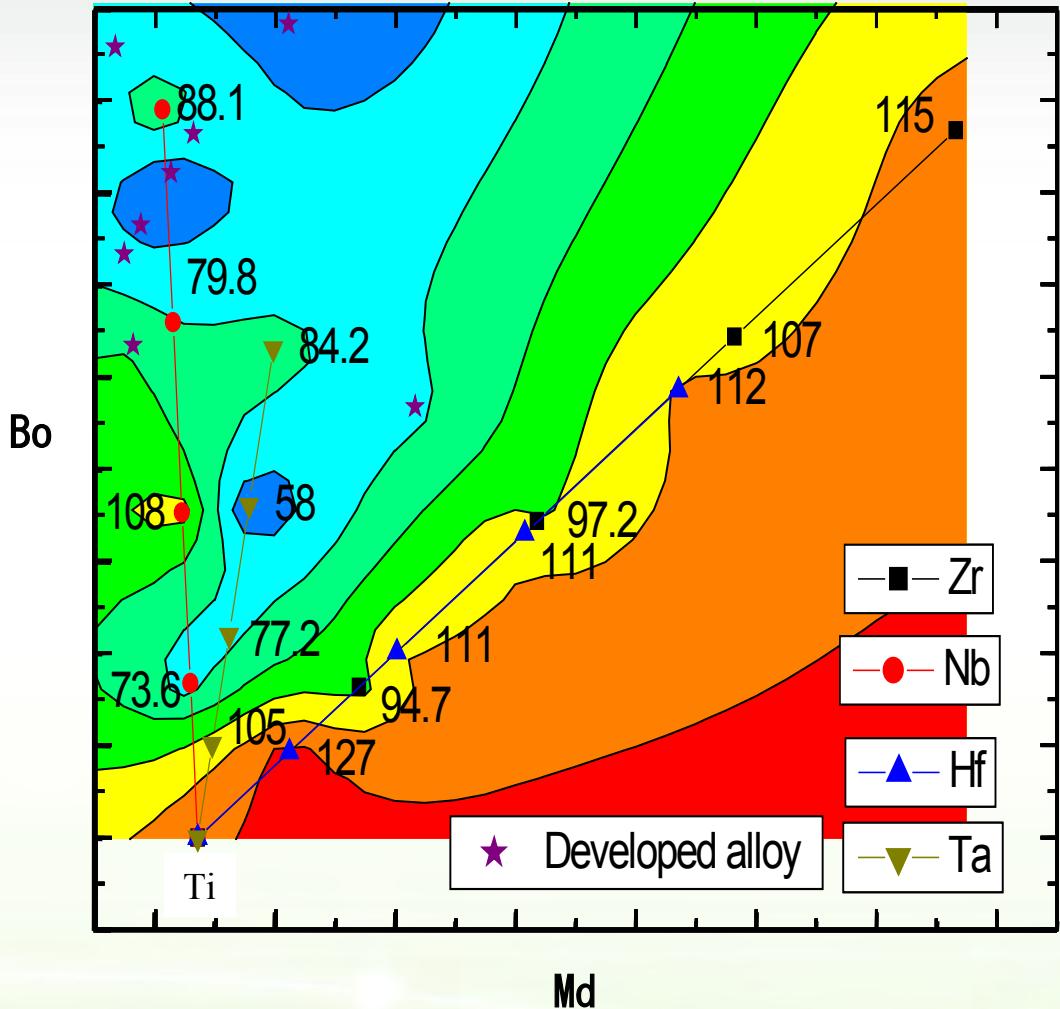
$$S_{ij} = \int \chi_i^*(l) \chi_j(l) dv_1$$

$$H(l) = -\frac{1}{2} \nabla_1^2 - \sum_v \frac{z_v}{r_{1v}} + \int \frac{\rho(2)}{r_{12}} dv_2 + v_{xc}(l)$$

By solving these equations, we can calculate electron density, electron number, then using these values, covalent bond strength between atomic orbital i and j in overlap population (Q_{ij}) can be calculated. Consequently, bond order of atoms showing covalent bond (Bo) and Fermi energy level of d-electrons (Md) can be determined.

Low Elastic Modulus Group on Bo-Md Map

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$$Bo = \sum [(P_{M-Ti,d})_i + (P_{Ti-Ti,d})_i]$$

$$Md = \frac{3E_{t2g} + 2E_{eg}}{5} - E_F$$

$$\overline{Bo} = \sum X_i Bo$$

$$\overline{Md} = \sum X_i Md$$

Bo : Bond Order

Md : d Electron Orbital Energy level

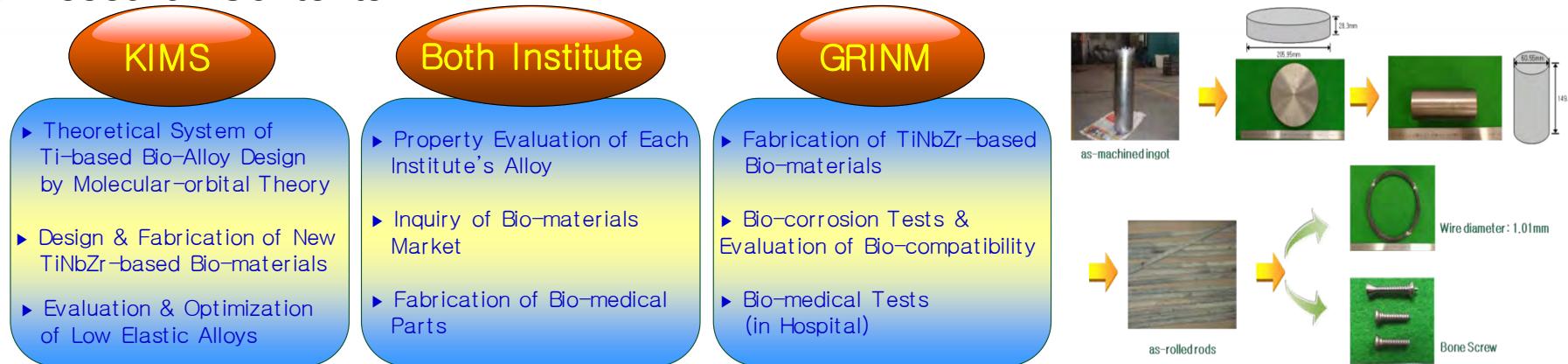
Titanium Alloy Design and Parts Development for Medical Implant

KIMS

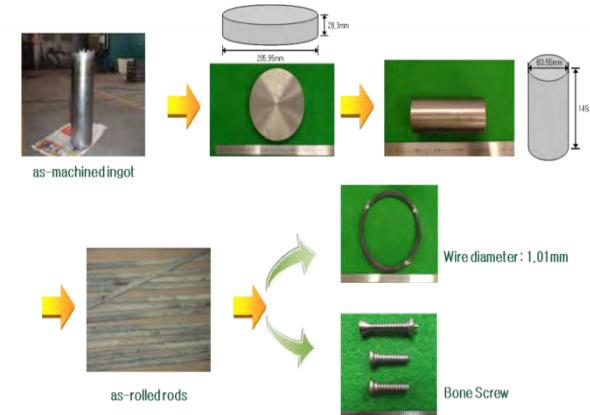
Research Purposes :

1. Alloy design of new β -based Ti alloy for bio-material parts
2. Titanium bio-materials with low elastic modulus (below 60 GPa) and excellent bio-compatibility, better formability

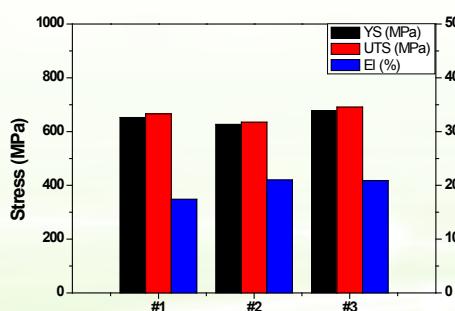
Research Contents :



Fabrication of new TNZ40 Alloy :

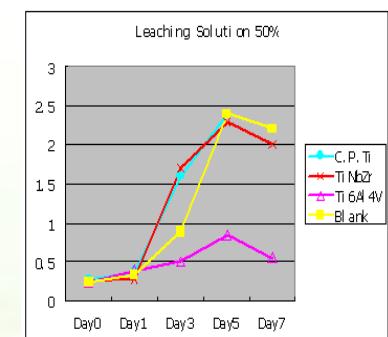
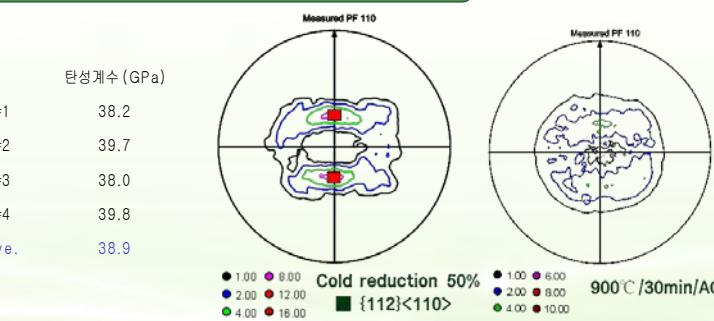


Development of Titanium Bio-medical Parts



1. Lee D-G, Lee Y.T., Mi, X.J., Ye W.J., Hui S.X.; Korea Patent, 10-0971649, PCT/KR2008/007693

2. Mi, X.J., Ye W.J., Hui S.X., Lee D-G, Lee Y.T. : 200810240992.X, □□, □ several patents/papers/presentations



Light absorption (OD value)

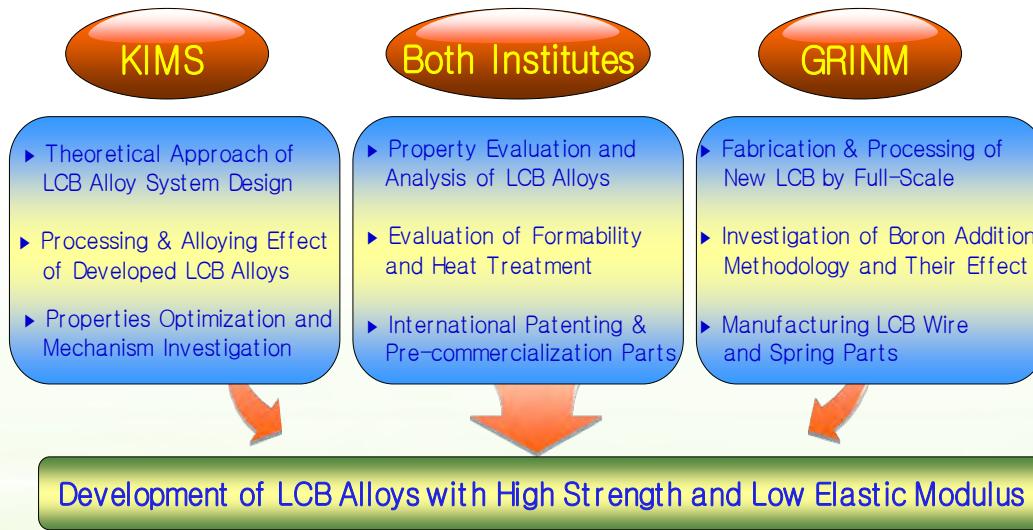
LCB Titanium Alloys

KIMS

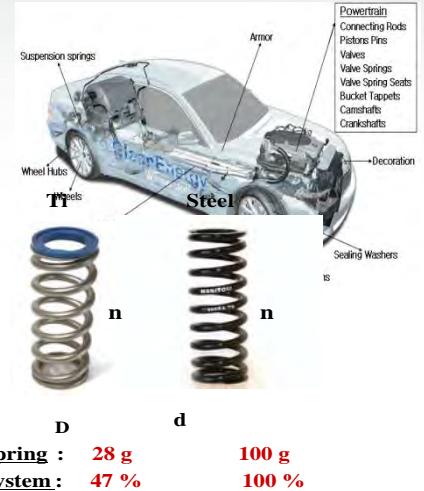
Research Purposes :

1. Development of the new beta titanium alloys having low elastic modulus and high strength by low cost alloying elements
2. Understanding of the alloying effect, microstructure evolution, strengthening mechanism and property optimization in the series of low cost beta titanium alloys
3. Development of a cost-effective material and processing method for automotive applications

Research Contents :



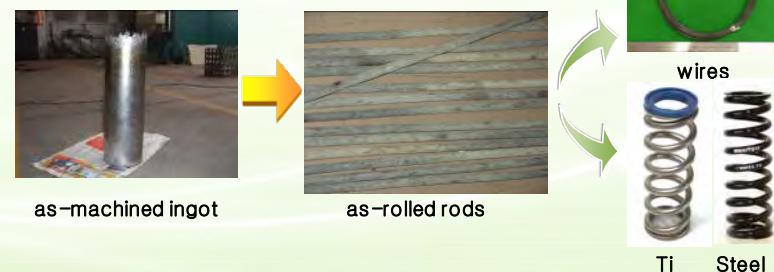
1. Lee D-G, Lee Y.T., Seo J.H. ; Korea Patent, 12-0057217, under PCT



Advantages :

Low Cost-Cheap Materials

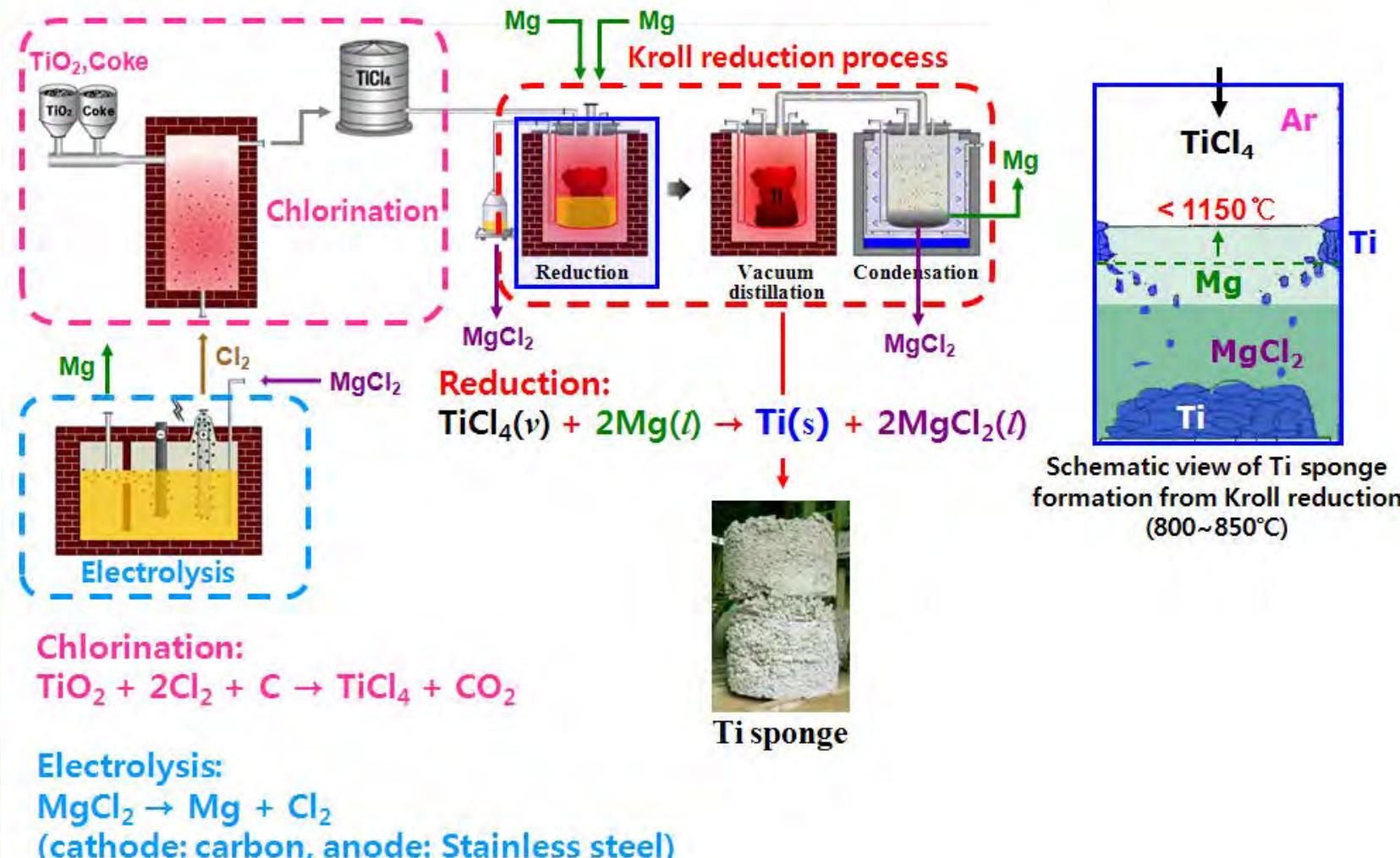
1. Low grade sponge
2. Cheap alloying element
3. Composition tolerance
4. Fabrication cost down
5. Mass production



Ti Steel

Kroll Process

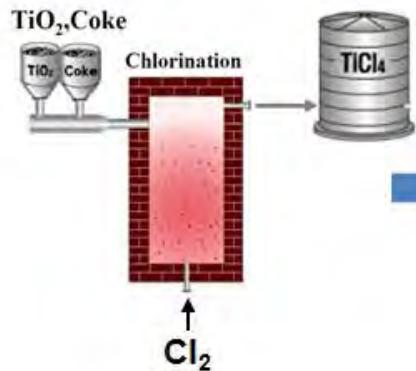
- Commercialized extraction process: >99% world Ti sponge production
- High productivity



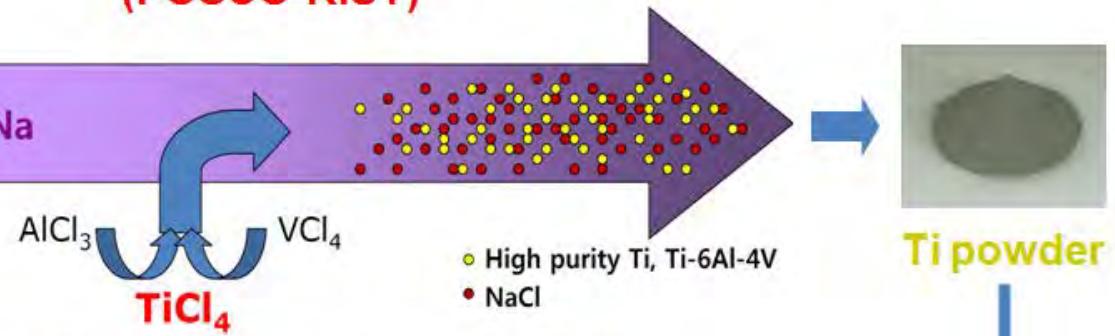
Direct Titanium Powder Process

KIMS

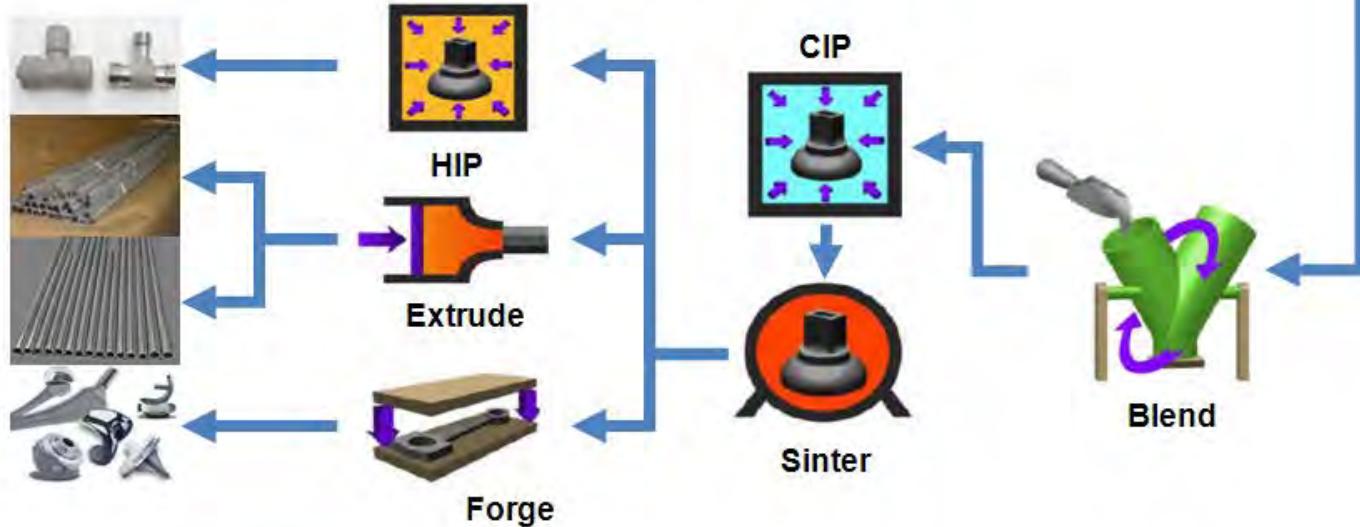
Millennium chemical (USA)



Armstrong process
(POSCO-RIST)



5kg/hr of production in 2015

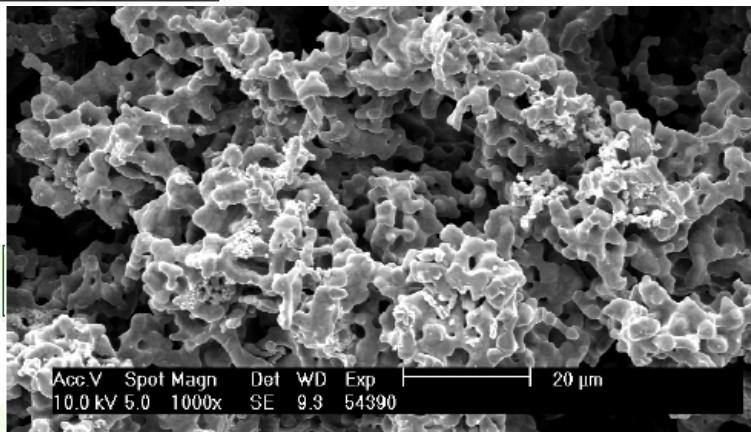
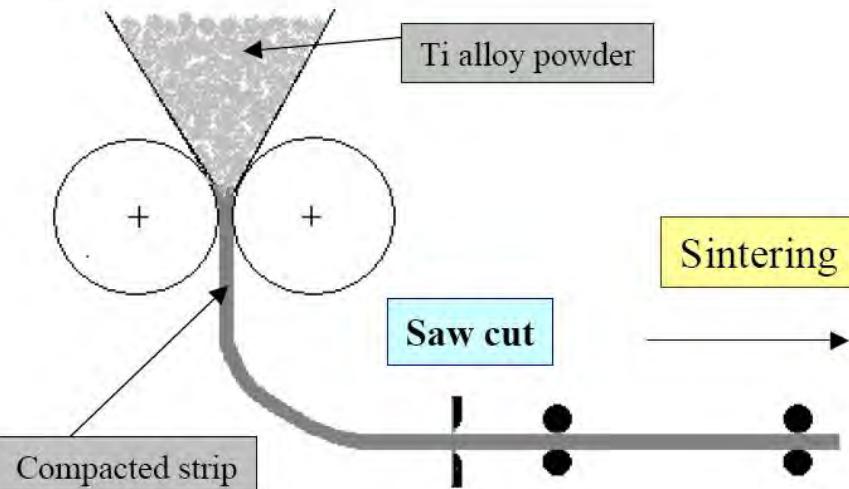


Direct Powder Rolling for Sheet

KIMS

Direct Powder Rolling

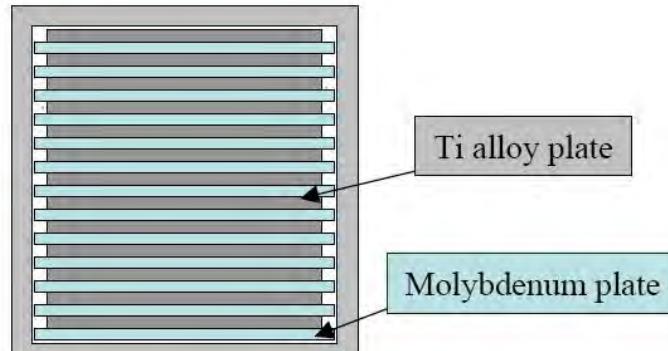
Powder rolling mill



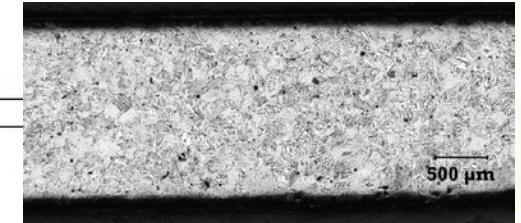
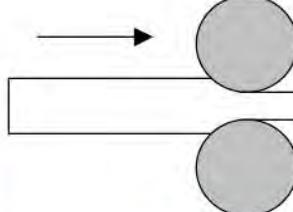
Materials Parameter: Purity, Size, Shape, Binder, Sinterability, etc.

Process Parameter: Roll Speed, Roll Gap, Roll Dia., Temperature, Humidity, etc.

Vacuum furnace



Re-rolling



Re-rolling mill

Titanium Precision Castings

KIMS



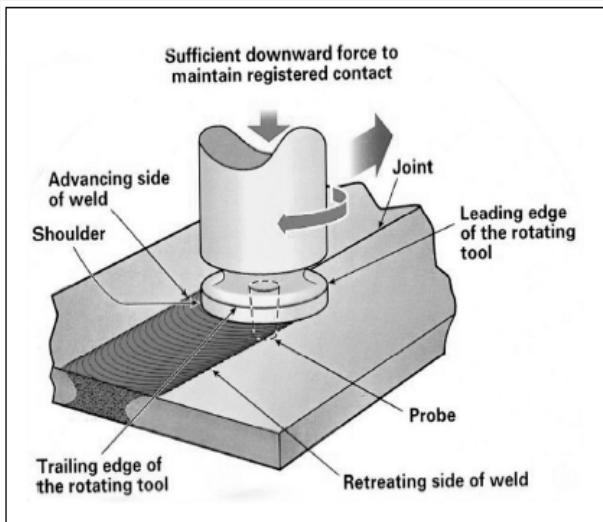
Titanium Ingot Defects and Causes

Processing	Origin of Defects	Type of Defects
Materials	<ul style="list-style-type: none">- Raw Materials<ul style="list-style-type: none">* Sponge Contamination* Recycled Titanium* Master Alloy Contamination* TIG Welding- Ingot<ul style="list-style-type: none">* Aggressive Grinding	<ul style="list-style-type: none">Type I (LDI, HID, HA)Type I , HDI (High Density Inclusion)Type IType I , HDIType I
Melting	<ul style="list-style-type: none">- Solidification<ul style="list-style-type: none">* Segregation* Microstructure* Shrinkage- Processing<ul style="list-style-type: none">* Air leak, Water leak* Arc Power Level Variation	<ul style="list-style-type: none">Type II (HAD) Beta fleck, Blocky AlphaLarge DendriteShrinking Pipe, PorosityType IType II, Beta Fleck, Blocky, Alpha
Forming	<ul style="list-style-type: none">* Heating Process* Microstructure* Strain rate* Oxide Inclusion* Super Cooling	<ul style="list-style-type: none">Alpha CaseElongated AlphaSIP (Strain Induced Porosity)Fold (Alpha case Folding)Crack in Corner

Solution of the Defects

Processing	Defects	Reasons	Solution
Solidification Defects	Type I	N, O	Raw materials Control, Triple melts
	Type II	Solidification Shrinkage	
	Blocky Alpha	Micro solidification	Triple melt, Top Cutting
	Beta Fleck	Segregation	Diffusion of the billet
	Dendrite	Local Heating, Over Heating	Diffusion of the billet
	Micro Shrinkage	In proper solidification	Egualized microstructure
	Micro Porosity	Local solidification	Shrinkage Mechanical Welding
	HDI	Ce, N, O	Raw material control
		W, Ta, WC, Nb	Screening the HMM
Processing Defects	Alpha Case	Oxidation	Shot Blasting, Chem-Milling
	Elongated Alpha	In Sufficient Recrystallization	Sufficient Plastic deformation
	SIP	Non uniform Deformation	Uniform microstructure
	Fold	Folding the Ingot	Die Design
	Corner Crack	Local Cooling	Edge cutting, Local Heating

Friction Stir Welding



- FSW was invented by W M Thomas in 1991 (International patent application PCT/GB92/02203)
- Over 1600 patents have been filed on FSW.
- About 10 FSW equipment manufacturers are licensed by TWI as at 16 May 2005.
- FSW can be applied in shipbuilding and marine industries, aerospace industries, railway industries, car industries, etc.

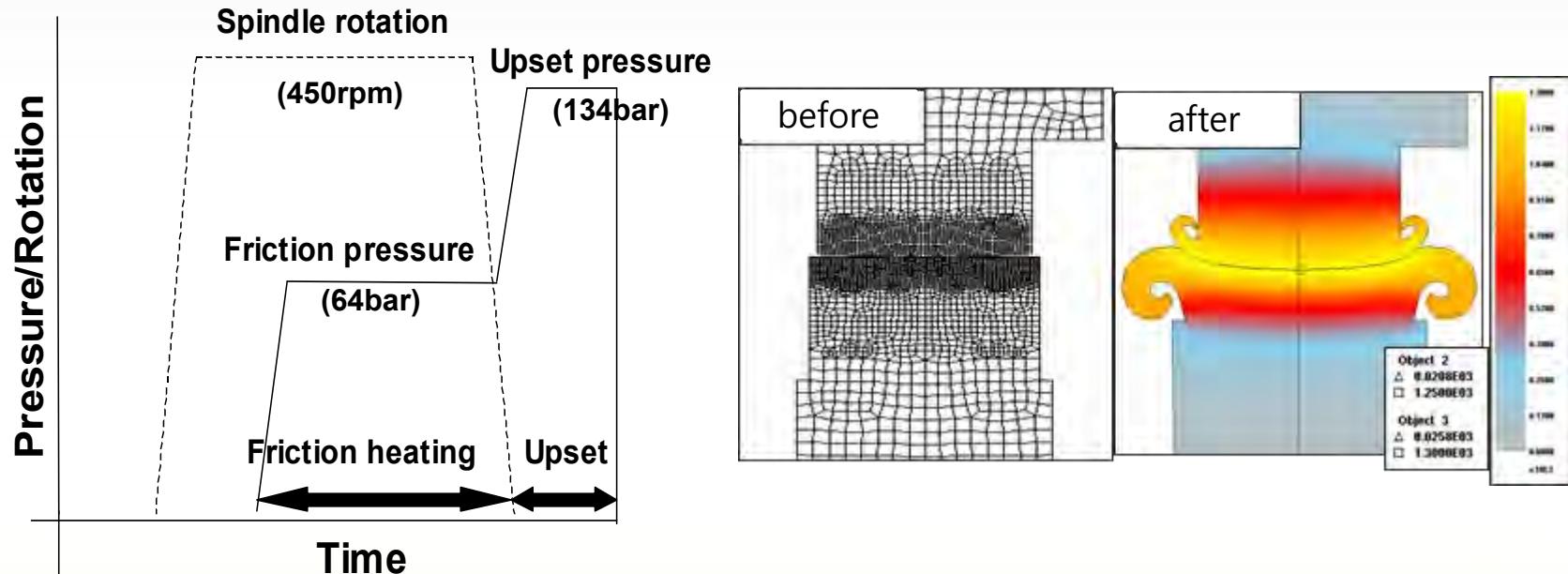
Process	Welding Speed (mm/min)	Power at Work kW	Gross Power Required (kW)	Heat Input kJ/mm
FSW	500	2	2.5*	0.24
MIG (Mech)	300	7.5	8.6	1.5
CO ₂ Laser	5000 1600	10 5	112 55	0.12 0.18

* - using a geared drive would increase value



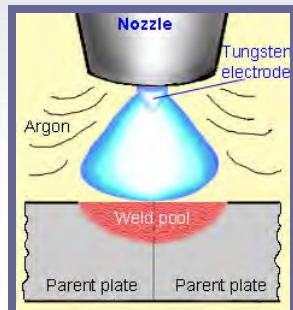
FSW of 6mm Ti-64 plate

Friction Stir Welding

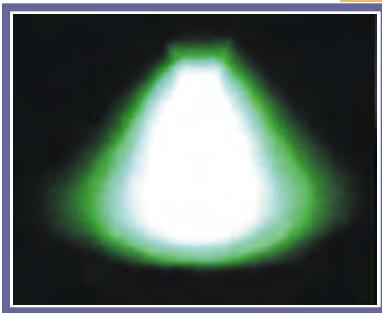
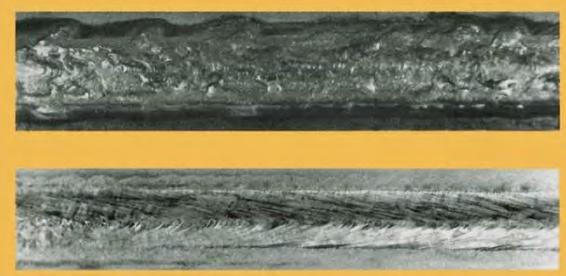


Properties	$(\alpha+\beta) - (\alpha+\beta)$	$(\alpha) - (\alpha+\beta)$	$(\beta) - (\alpha+\beta)$
YS (MPa)	888.24	378.58	880.05
UTS (MPa)	958.13	509.38	883.72
EI (%)	17.7	20.5	19.3

Titanium Welding with Flux



TIG-F

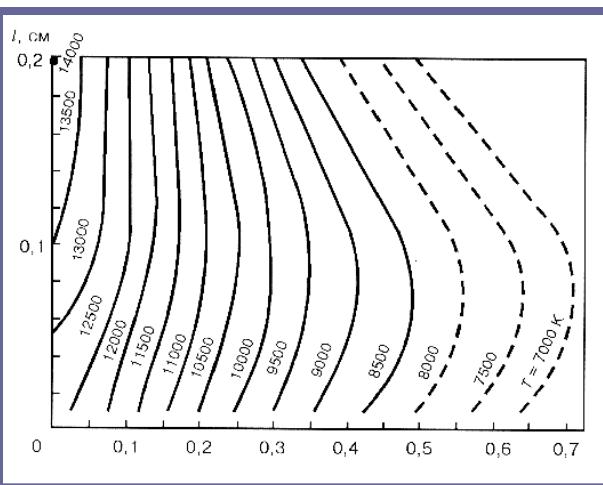
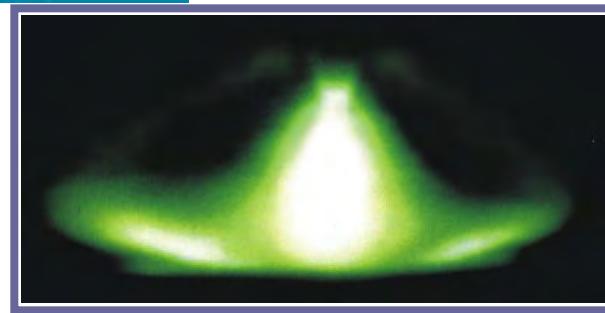
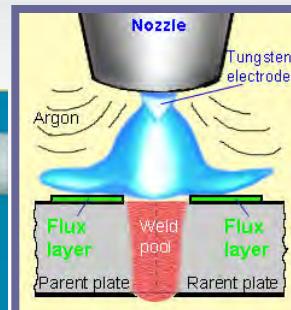
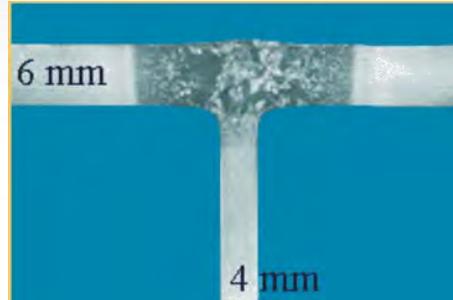


Video picture of the arc

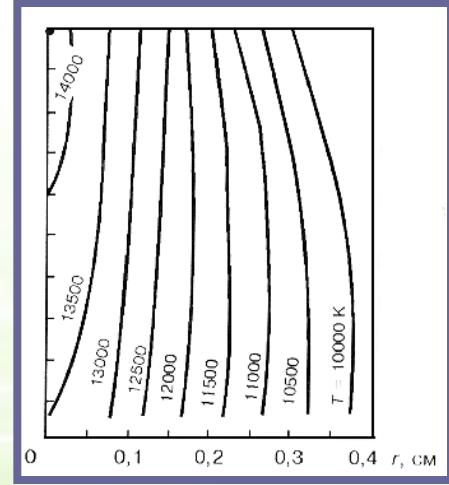
a – without flux

b – with flux

TIG-FW

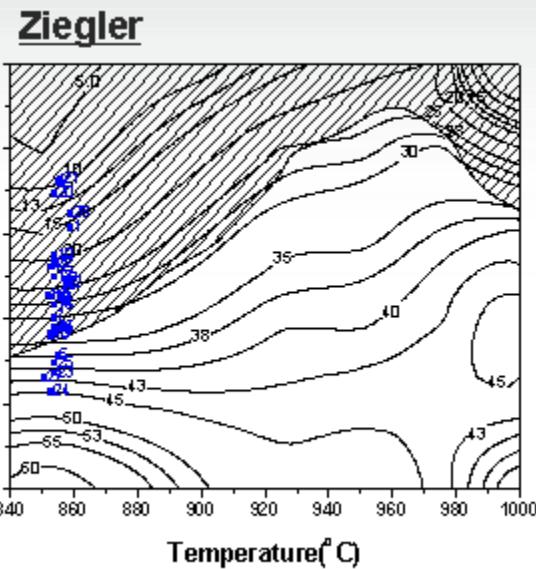
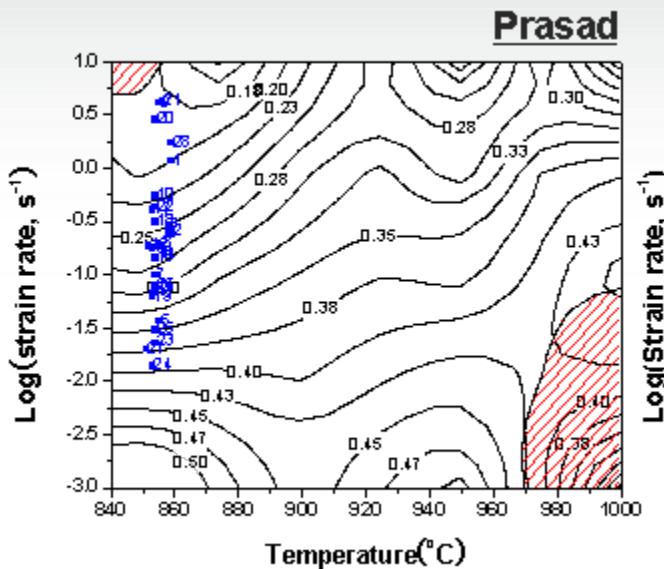


Distribution of temperature across the arc axis

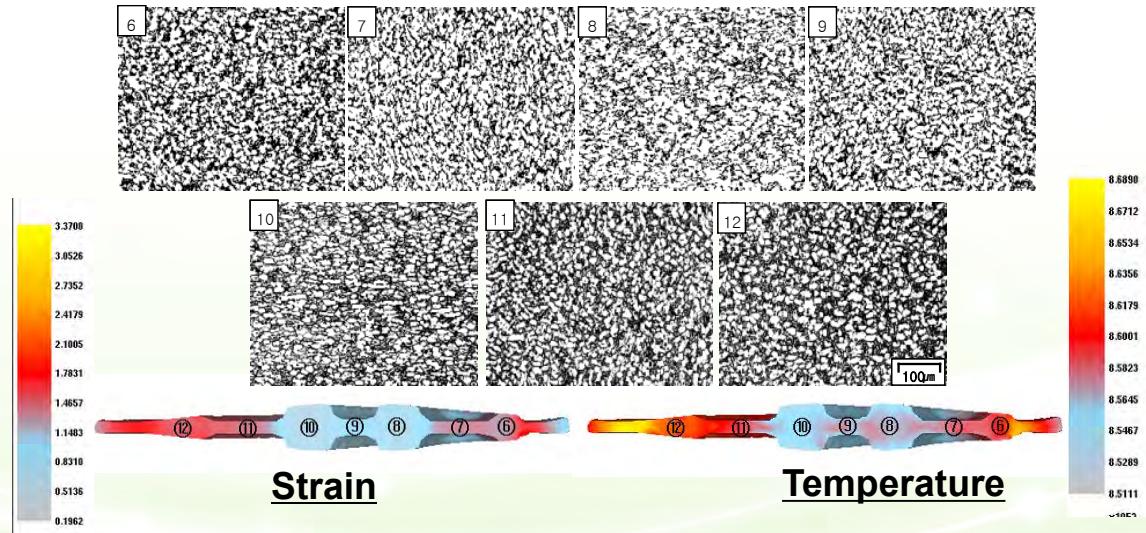
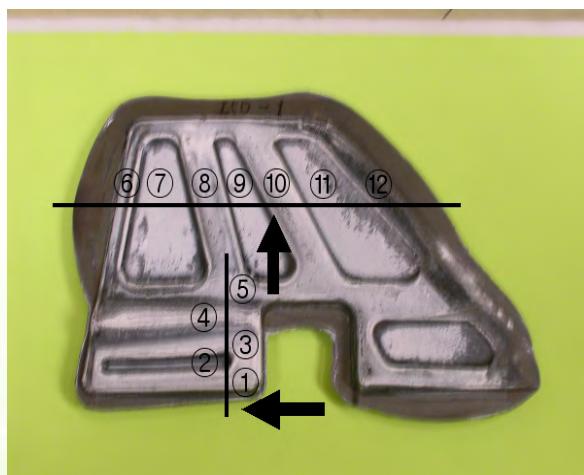


Titanium Alloys Isothermal Forging

KIMS



- mold temp. : 850°C
- mat. temp. : 850°C
- ram speed : ~1mm/s



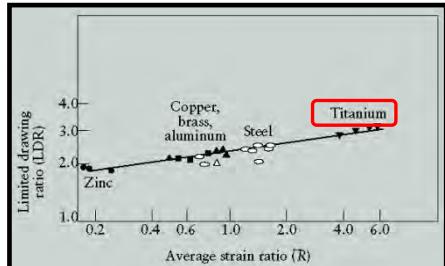
Precision Forming of Titanium Alloys

KIMS

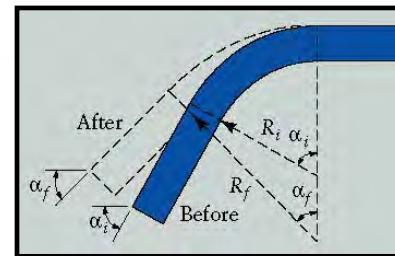
Work Scope

1. Process Windows for Sheet Metal Forming of Titanium Metals and Alloys
2. Characterization and Enhancement of Sheet Metal Formability of Titanium Alloys

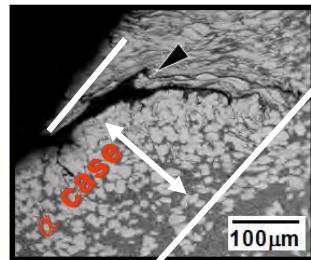
Anisotropic Deformation Behavior



Spring back



Formation of α Case and Surface Crack



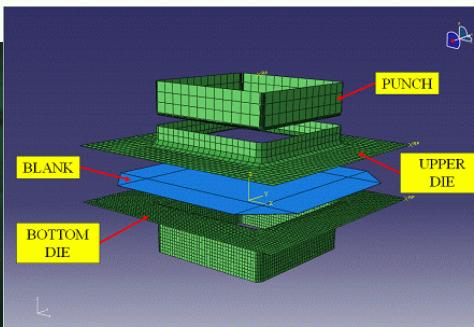
Sticking with Dies



Deep Drawing of Ti- 64 Alloys Sheets



Hot sizing & Descaling

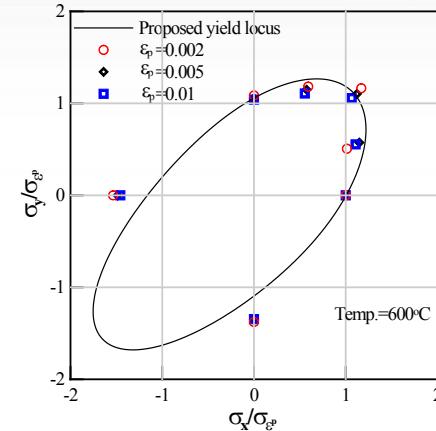
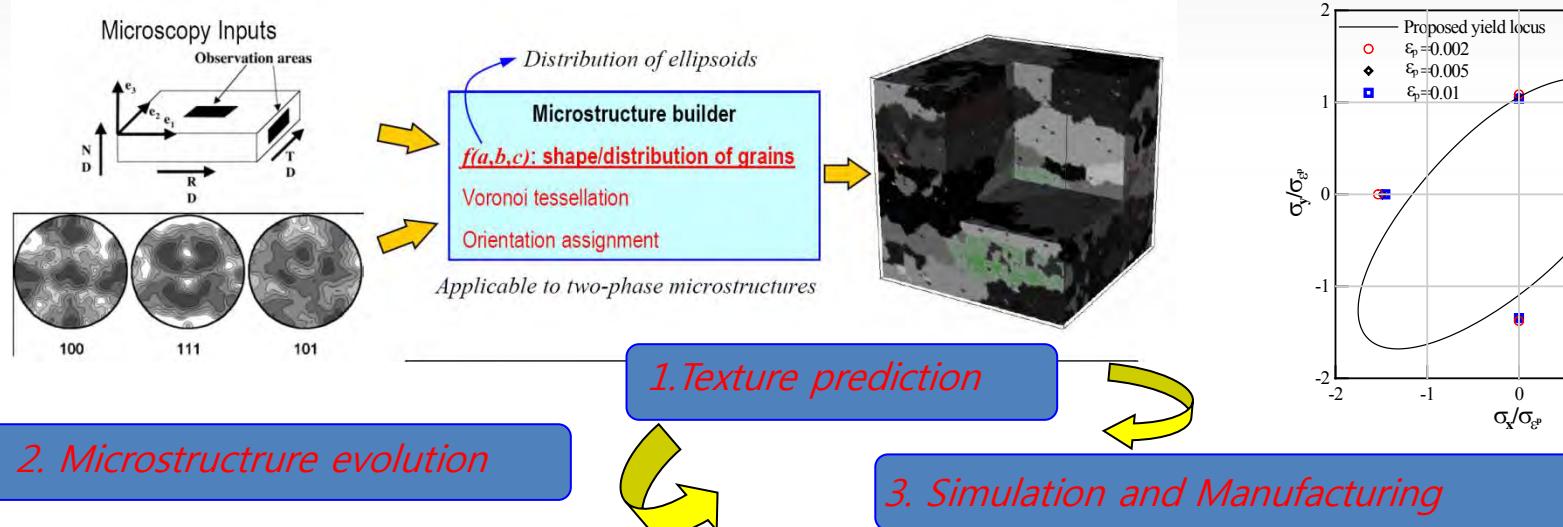


Precision Forming of Titanium Alloys

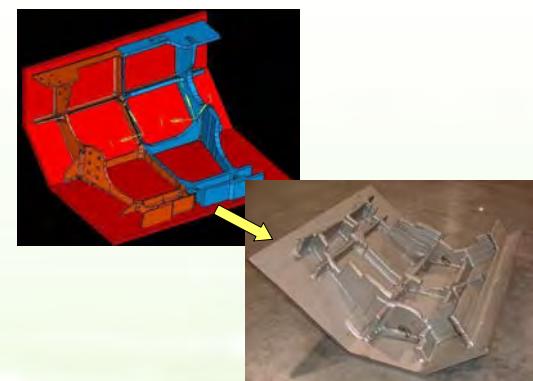
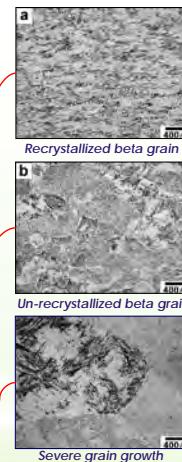
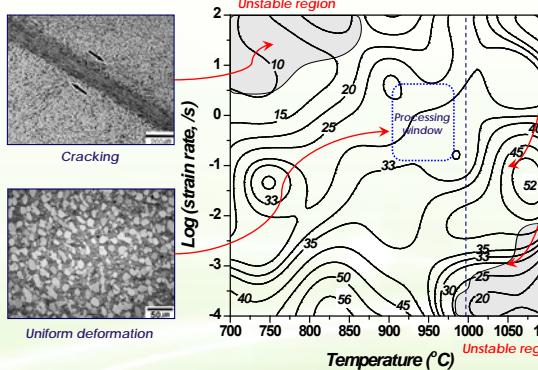
KIMS

Work Scope

- FE Simulation of anisotropic deformation behavior and microstructure evolution



Process Optimization



Isothermally Forged Part

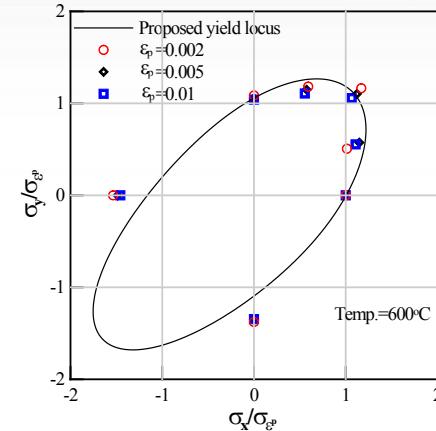
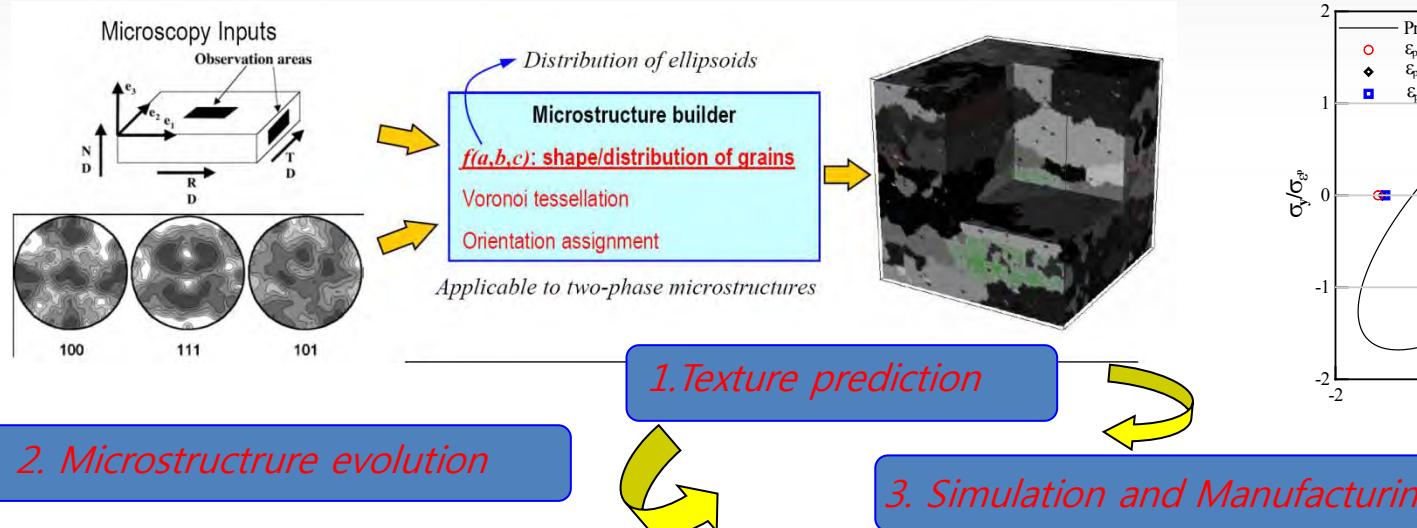


Precision Forming of Titanium Alloys

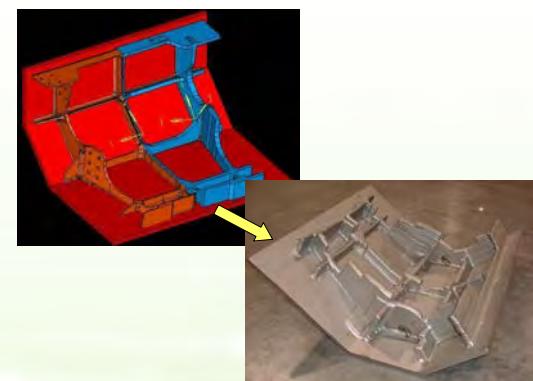
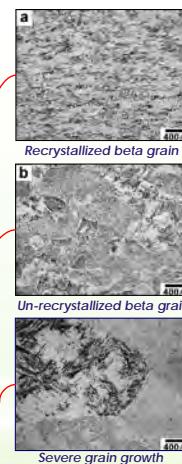
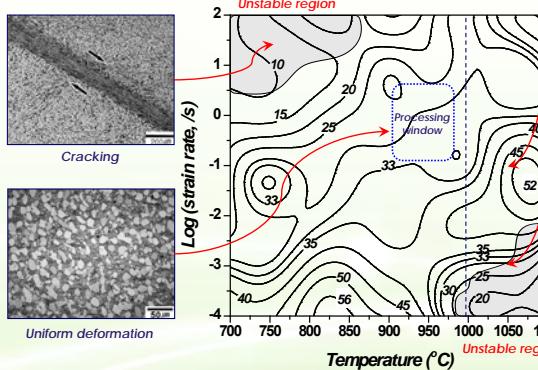
KIMS

Work Scope

- FE Simulation of anisotropic deformation behavior and microstructure evolution



Process Optimization



Isothermally Forged Part



Development of UFG Ti alloys without SPD

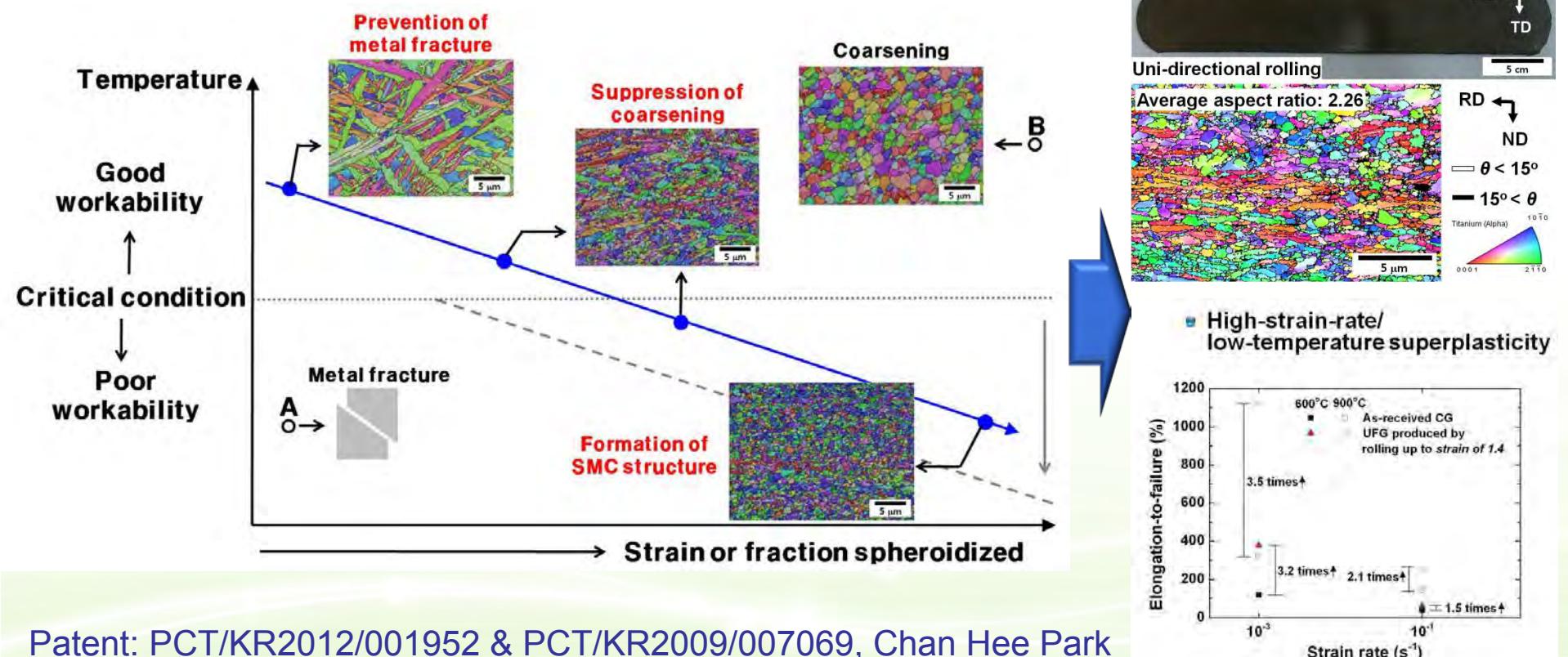
KIMS

Research Purposes :

1. To control an UFG microstructure using lower strains and higher strain rates
2. To fabricate UFG Ti alloys using conventional metal forming methods
(rolling, extrusion, forging etc.)

- Grain size ~ 400 nm
- Imposed Strain ~ 1.4
- Strain rate $\sim 0.1/s$

Schematic illustration of novel process (Ti-6Al-4V)

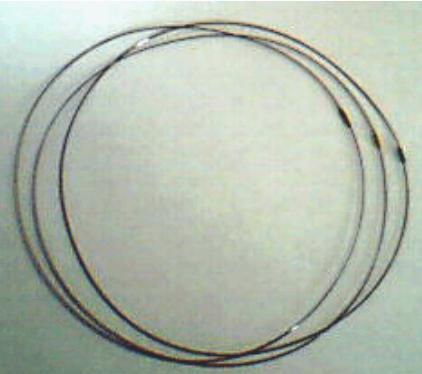


Superelastic NiTi thin wire for medical device

KIMS

Research Purposes :

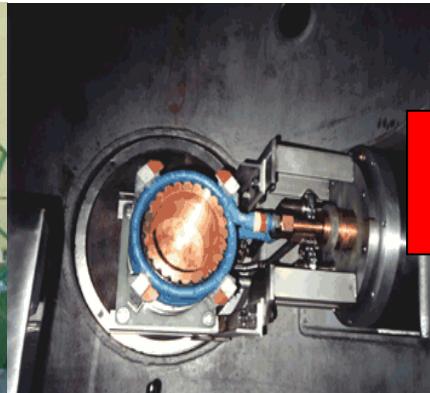
1. Superelasticity NiTi wire with a diameter of 0.1 mm by thermo-mechanical process
2. Development of high purity NiTi ingot using VAR skull/VAR process



Compositional deviation of Ni element: within 0.5% wt.
Oxygen and Carbon less than 0.1% wt.
Diameter: ~0.1 mm, Total elongation: >10%
Tensile strength: > 1150 MPa

Research Contents :

Vacuum Skull Melting



Vacuum Arc Re-melting



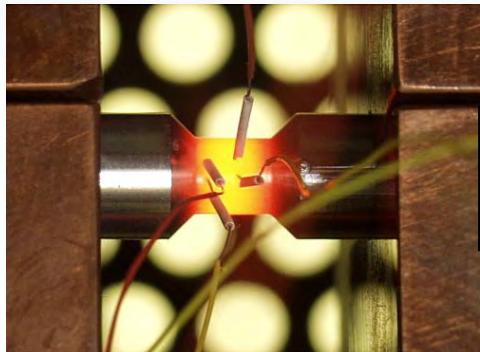
- Capacity : 3kg melting & casting
- Centrifugal caster : 400 rpm

- Ingot dimension : 200mm(dia) x 800mm (length)

Superelastic NiTi thin wire for medical device

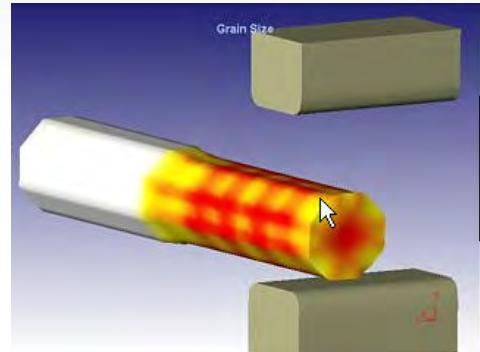
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Gleeble Test Machine



- Basic mechanical property acquisition

FE analysis for Ingot breakdown



- Design of thermo- mechanical process

Wire drawing



Development of TiNi and CoCr Precision Tube for Medical Implants (New project)

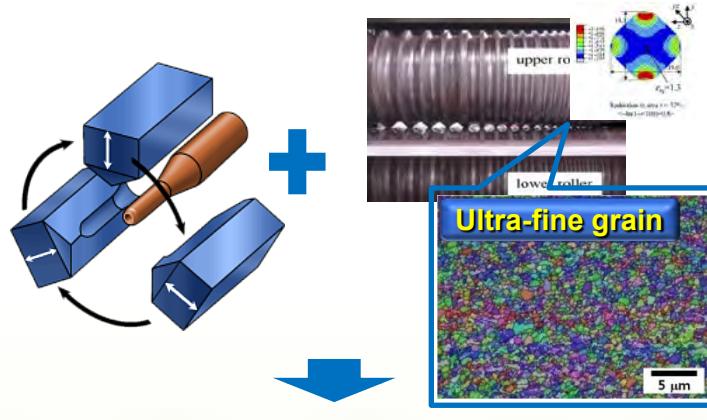
KIMS

Research Purposes :

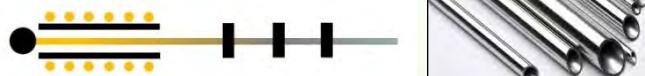
- Development of TiNi and CoCr precision tube for medical implants using the combination approach

Research Contents :

Tube Manufacturing Technology

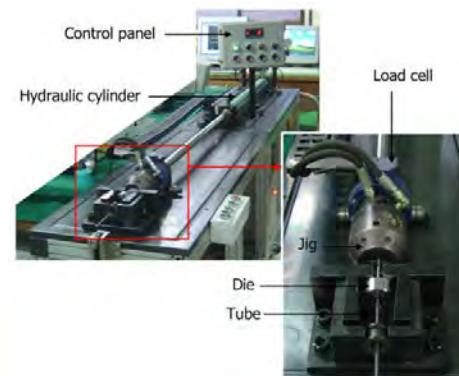


Warm or cold tube drawing



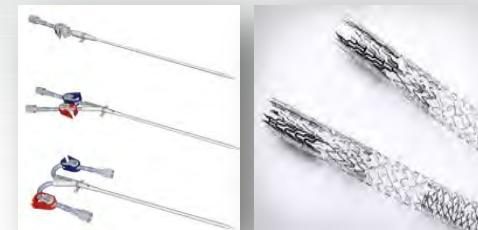
- ◆ Combination Technology :
Swaging + Caliber rolling
⇒ **grain refinement**

Tube Drawing



- ◆ Design of **precision tube drawing equipment**

- ◆ **Bi-metal tube drawing**



End Product



High purity billet Precision tube



Medical devices

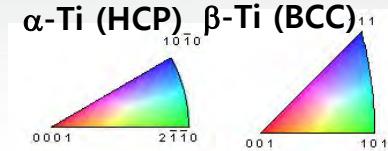
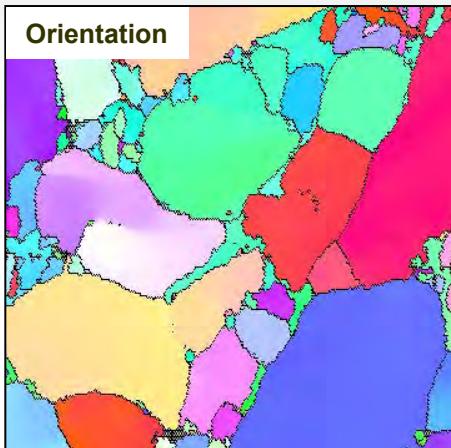
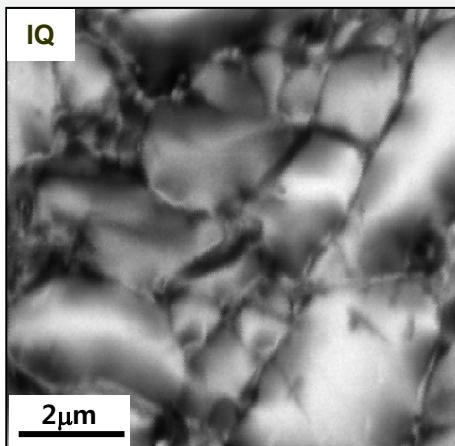


Stent

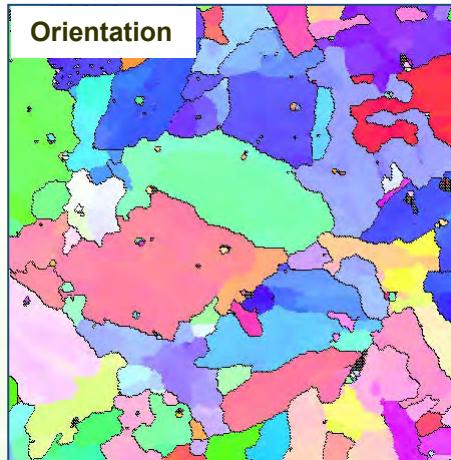
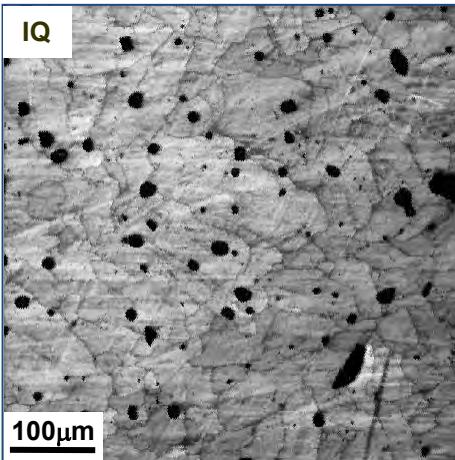
EBSD analysis of Titanium Alloys

KIMS

● ($\alpha + \beta$) alloy : Ti-6Al-4Fe-0.25Si

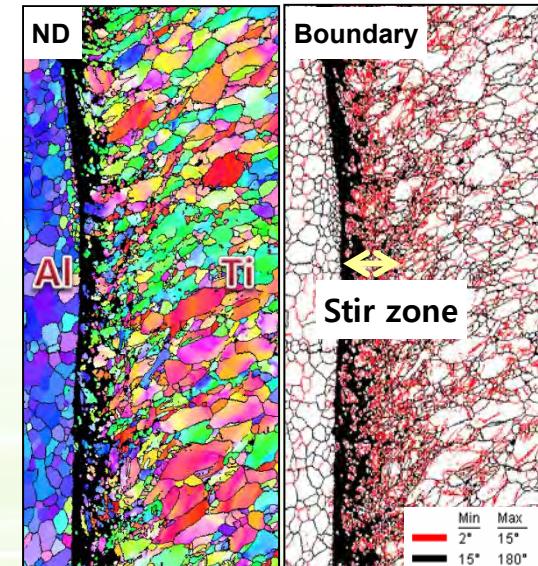


● Powder Rolled Titanium



Porosity : 3.4%

● Friction Stir Welded Ti-Al



1. Song, Y.H. et al., Korean J. Met. Mater., 50 (2012), To be published.

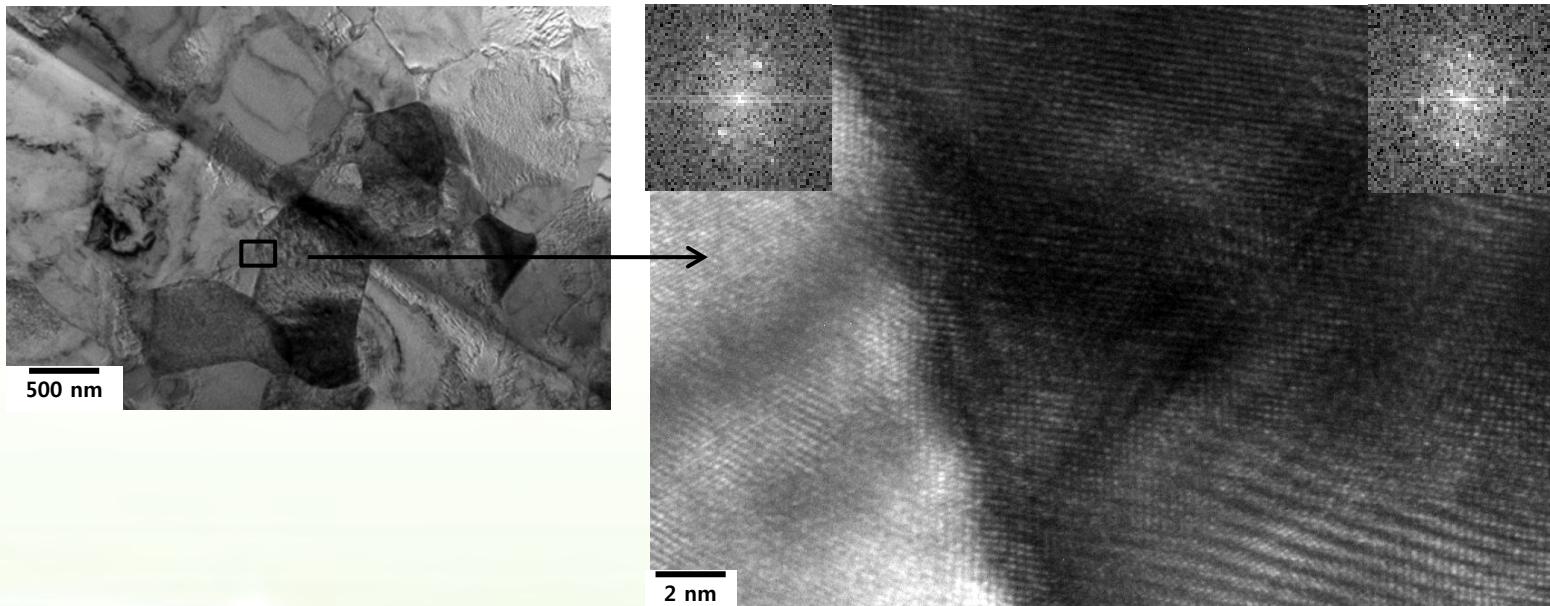
2. Kang J.-H. et al., IWJC 2012 (2012).

● Research Purposes :

1. Understanding microstructure after deformation at R.T. and high temperature ($\sim 700^{\circ}\text{C}$)
2. Identification of precipitate (TiFe) during aging at different time and temperature.
3. Finding out crystallization condition of TiNi thin films for SMA application

● Research Contents

1. Microstructure after deformation at 700°C of Ti-6Al-4Fe alloy



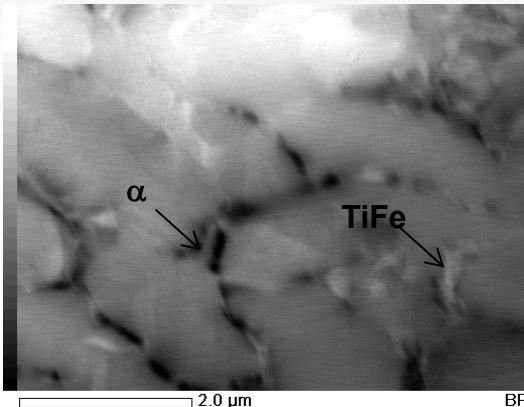
High angle grain boundaries with reduced grain size after deformation

In-situ and Ex-situ TEM Observations of Titanium Alloy (Ti-6Al-4Fe-0.25Si and TiNi thin films)

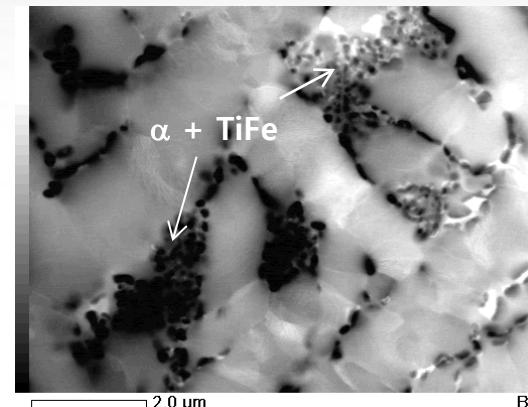
KIMS

Research Contents

2. Precipitate formation and growth during aging at 550°C



TiFe formation after 10h



Increased TiFe fraction after 100h

3. In-situ heating TEM observation of TiNi thin films

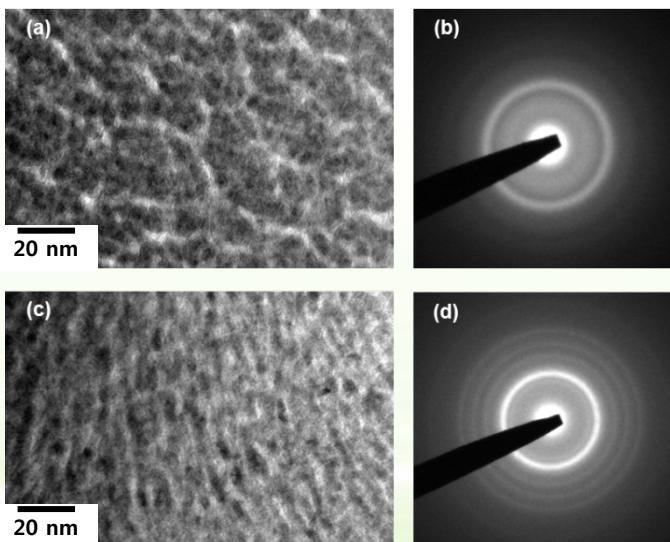


Fig. (a, c) Microstructures and (b, d) SADP of Ti-50.1Ni thin film by TEM (a, b) as-deposited and (c, d) after annealing at 500°C for 30 min. SADPs indicate that as-deposited film was amorphous structure (b) and fully crystallized after annealing (d).

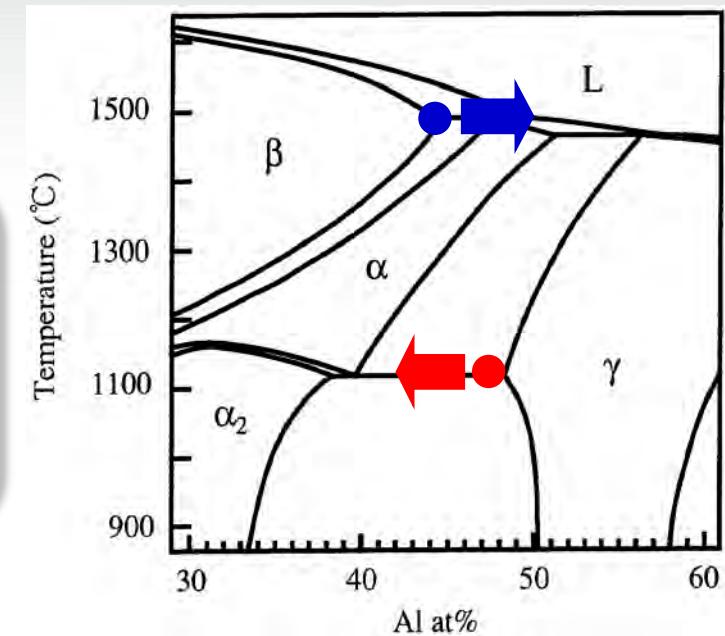
Development of Beta-Gamma TiAl

KIMS

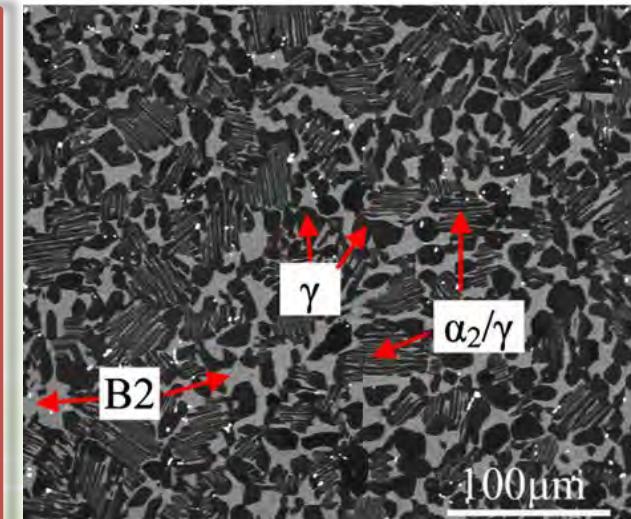
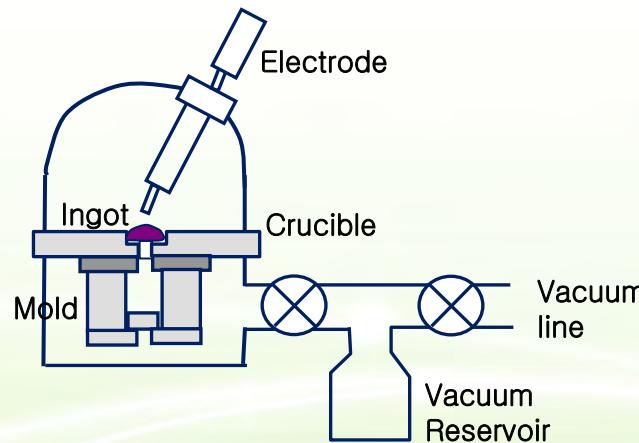
New alloy design : TiAl-xNb-yW-zC

➤ Effect of alloying elements

1. **Nb** : Oxidation resistance, Formability
2. **W** : Beta phase stabilizer (more effective than Mo, V)
3. **B, C** : grain size refinement

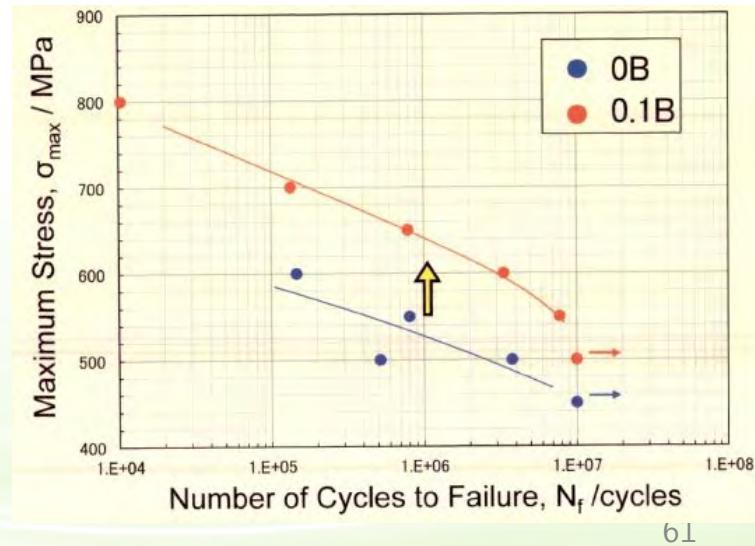
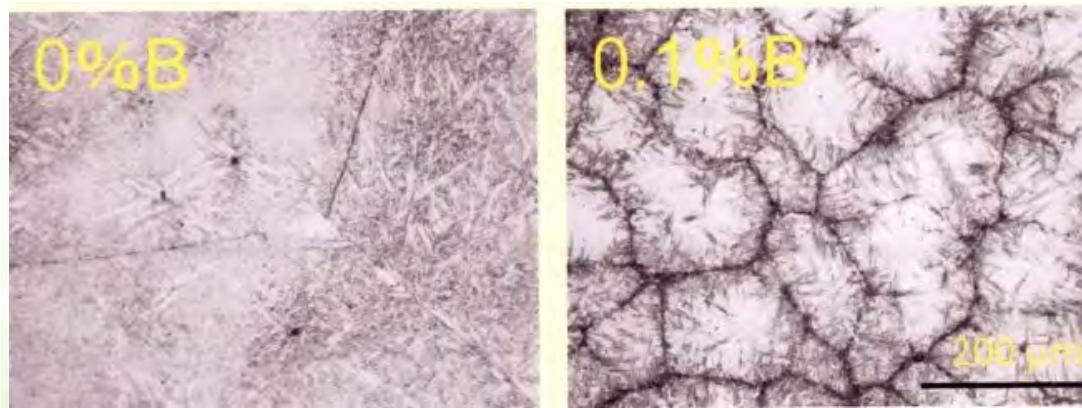
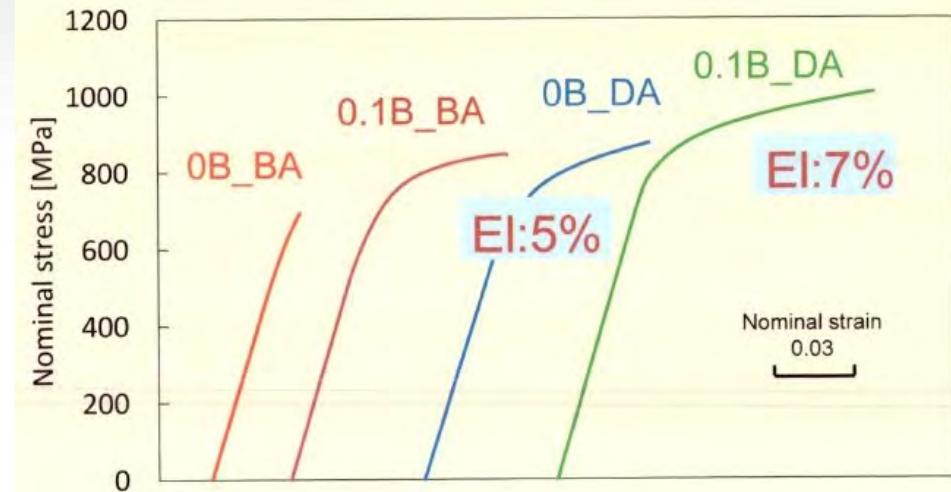
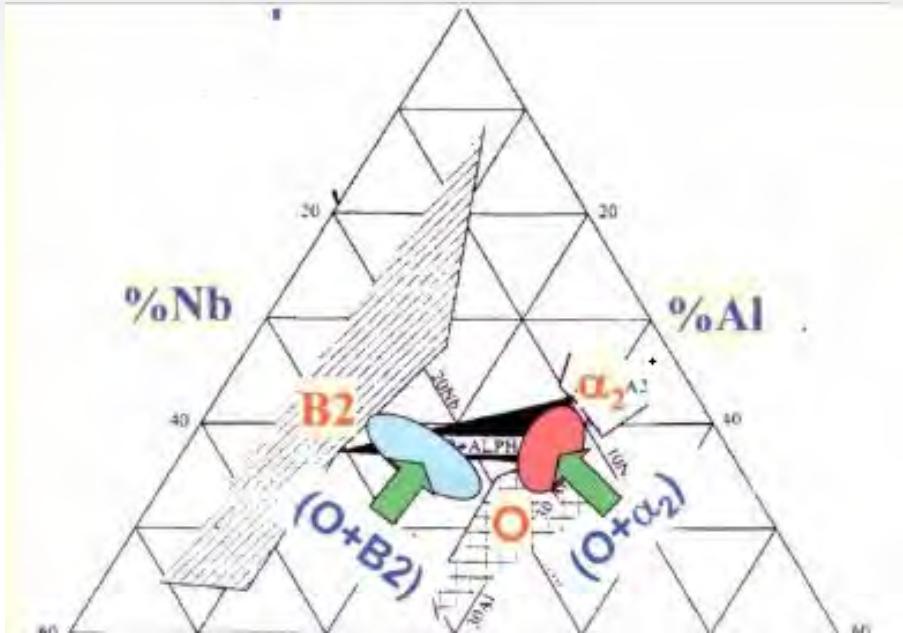


Target : UTS > 800 MPa, Ductility > 2.5%



Intermetallics - O Phase

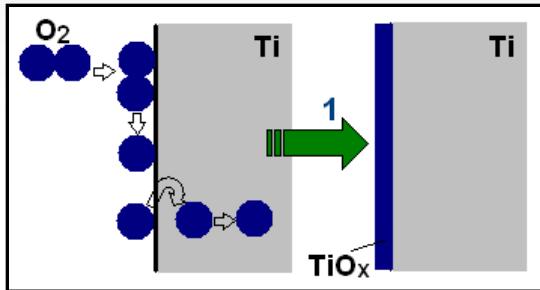
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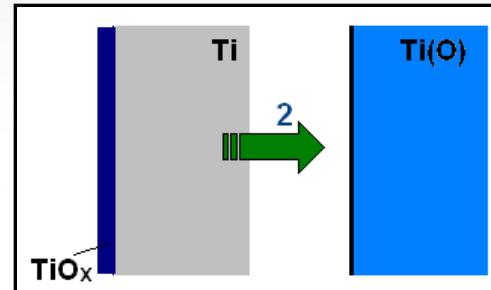
Mechanism of Surface Hardening

KIMS

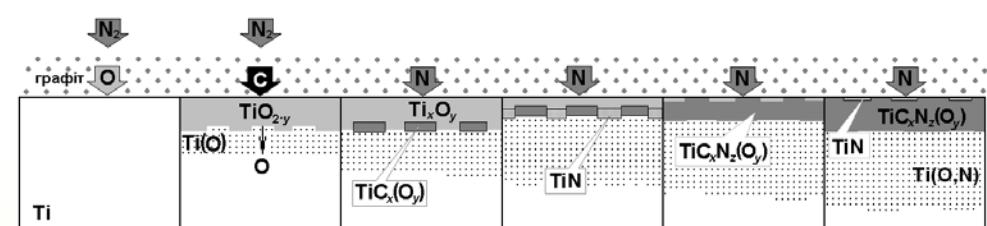
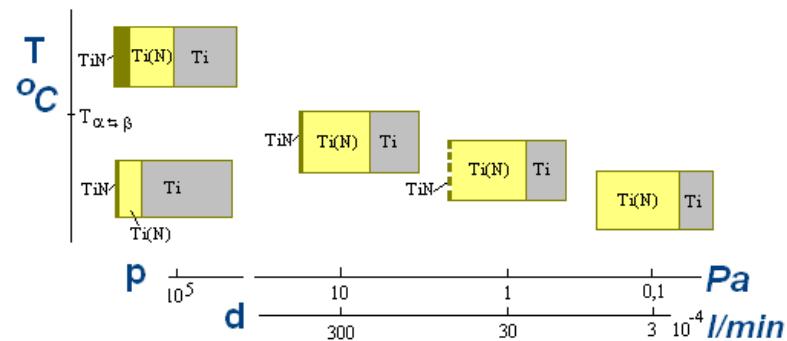
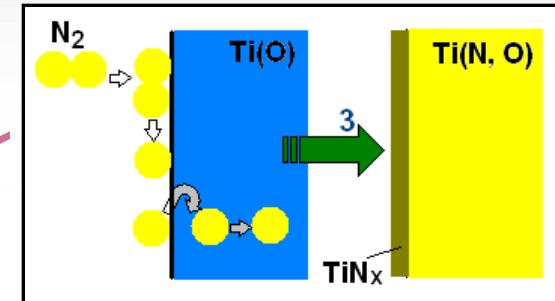
Surface oxide film formation



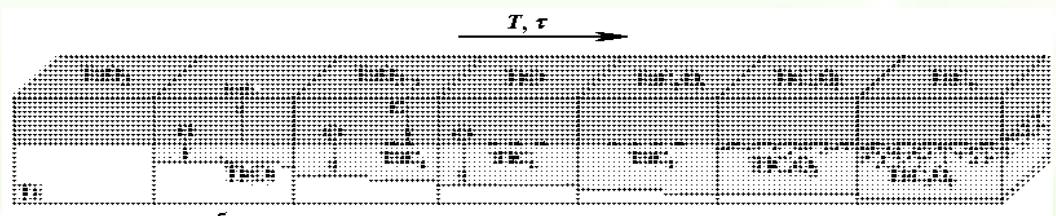
Oxide film dissolution



Nitride film formation



Ti-C-N system



Ti-C-O system