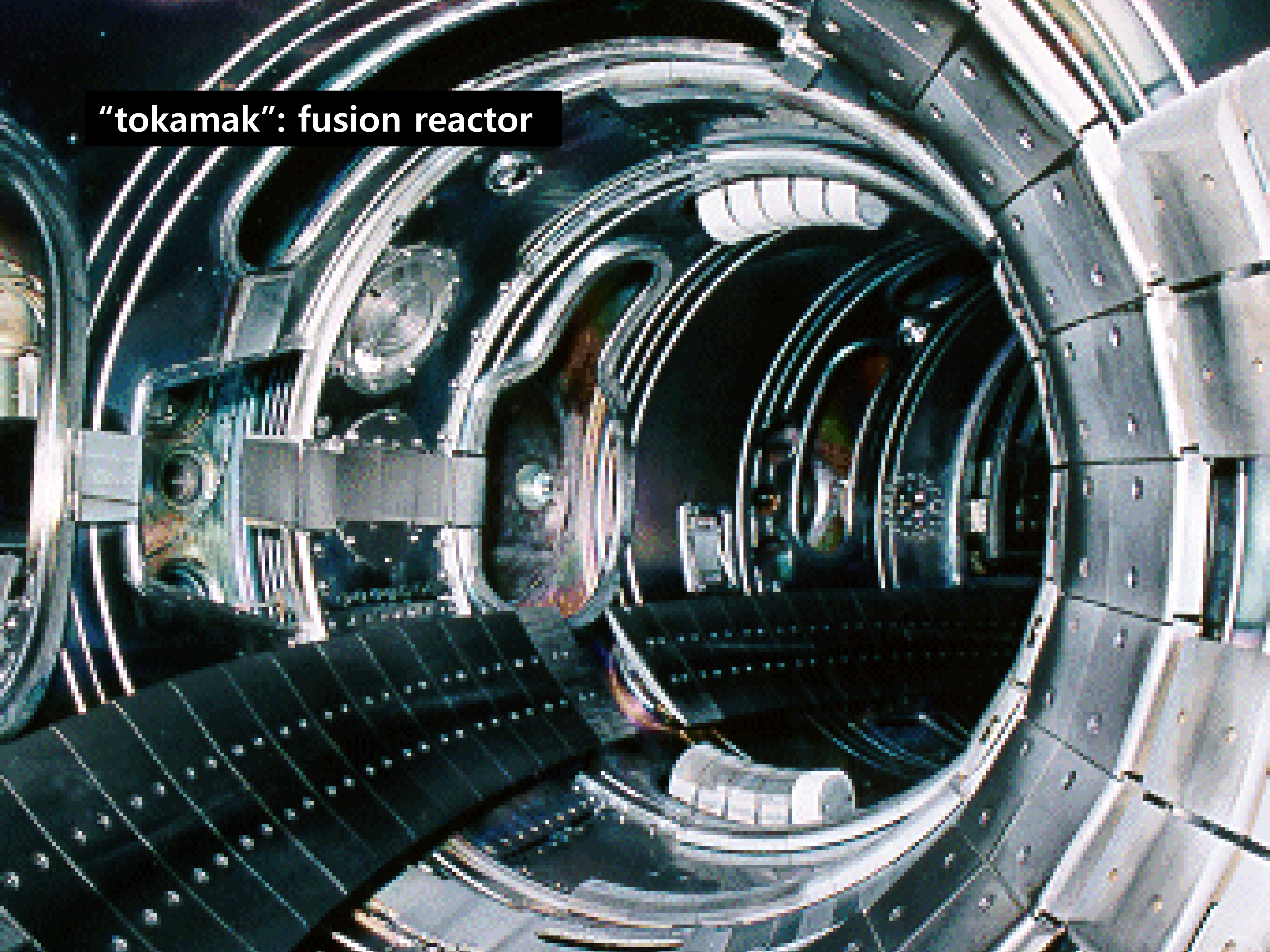
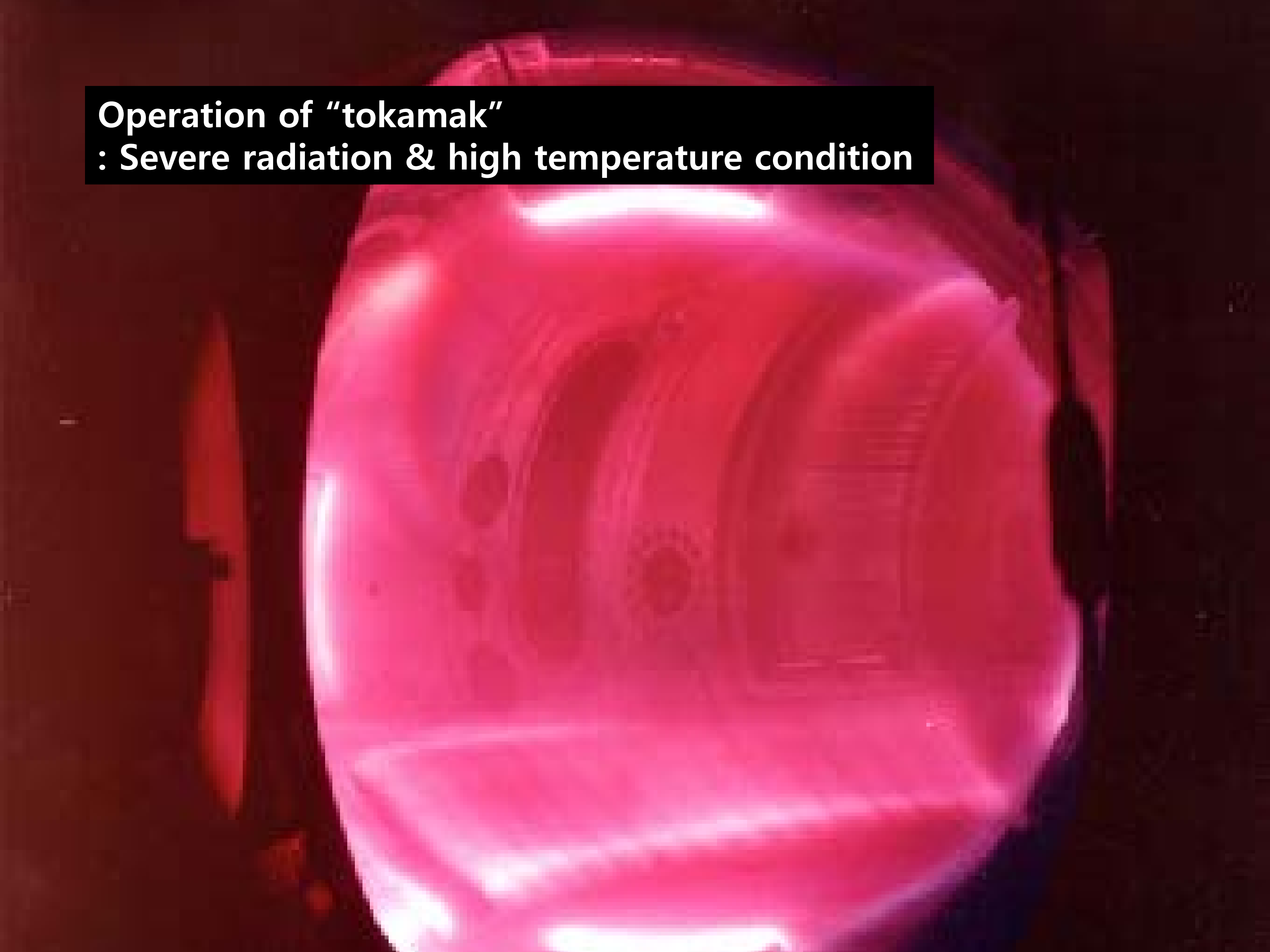
Tungsten Alloys as a Structural Materials in Extreme Environment

2017. 03. 13

ESPark Research Group
Il Hwan Kim



“tokamak”: fusion reactor



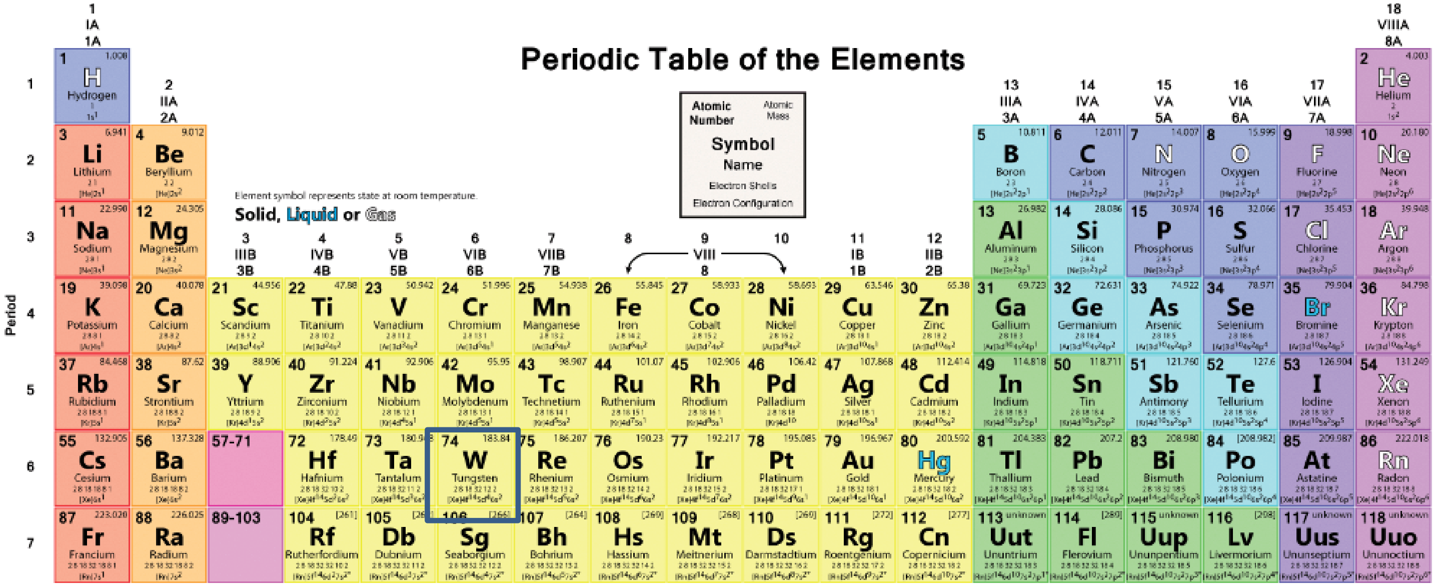
Operation of "tokamak"
: Severe radiation & high temperature condition

Contents

1. Introduction:

Requirements and Design Concept of Tungsten alloys

Characteristics of Tungsten Element



Periodic Table of the Elements

Atomic Number | Atomic Mass | Symbol | Name | Electron Shells | Electron Configuration

Element symbol represents state at room temperature.

Solid, Liquid or Gas

Period	1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1	1 H Hydrogen 1.008																	2 He Helium 4.003
2	3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
3	11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminium 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
4	19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
5	37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.249
6	55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
7	87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [26	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

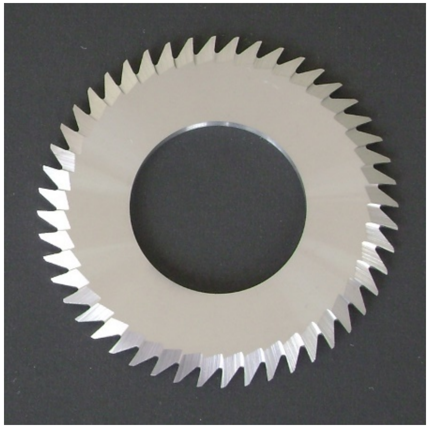
VIB

74

W

183.84

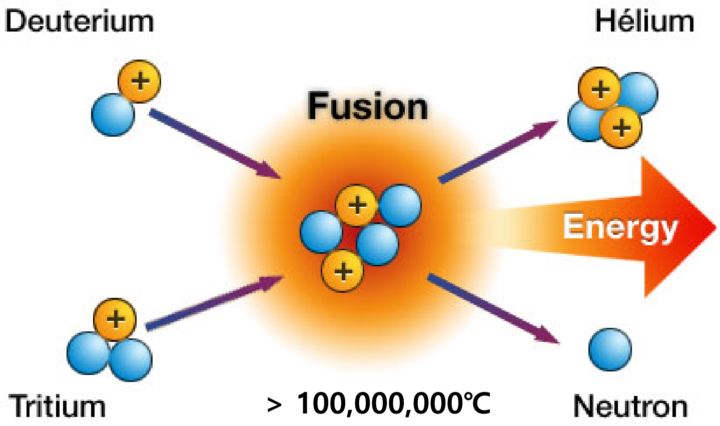
- **Transition Metal**
- **Crystal Structure: BCC**
- **Density: 19.25g/cm^3**
- **Melting Point: 3422℃**
- **Thermal Conductivity: 173W/m-K**



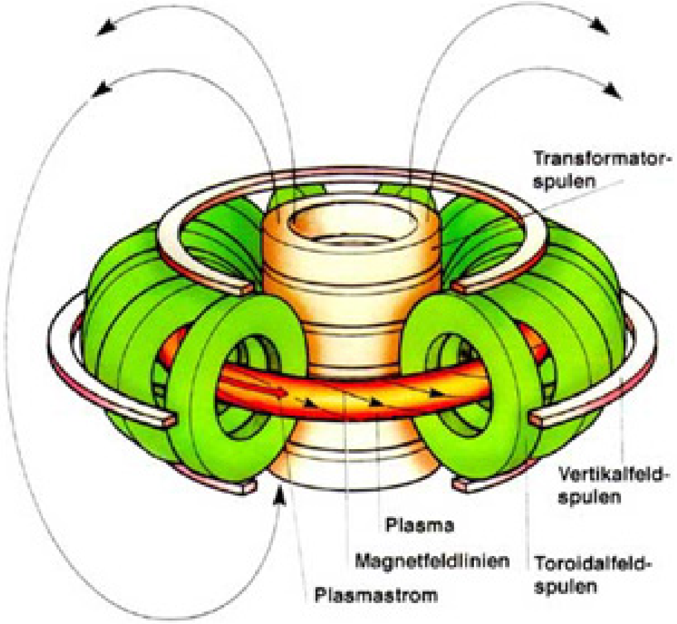
One of the most promising candidates for fusion reactor materials!

Fusion Reactor as a Future Energy Source

Fusion Reaction



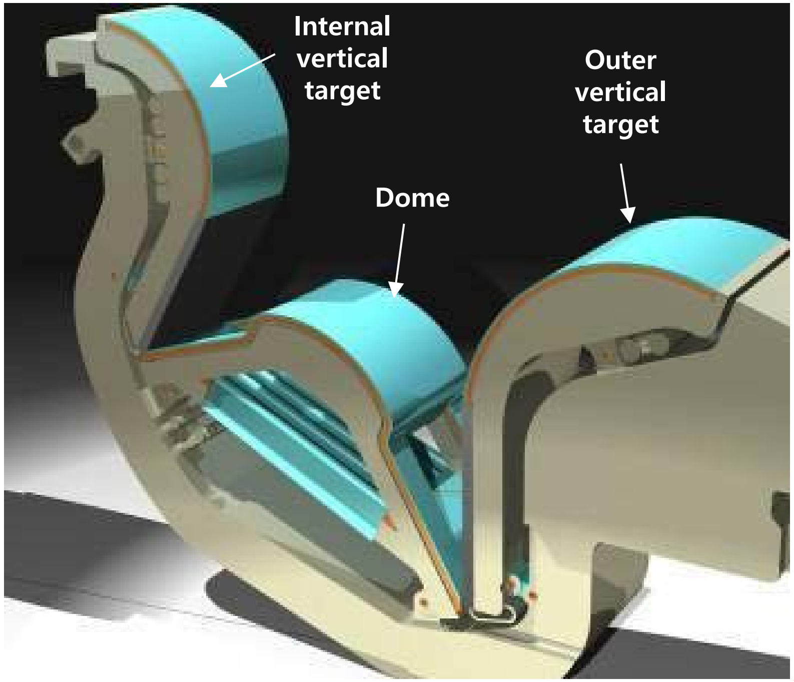
Tokamak



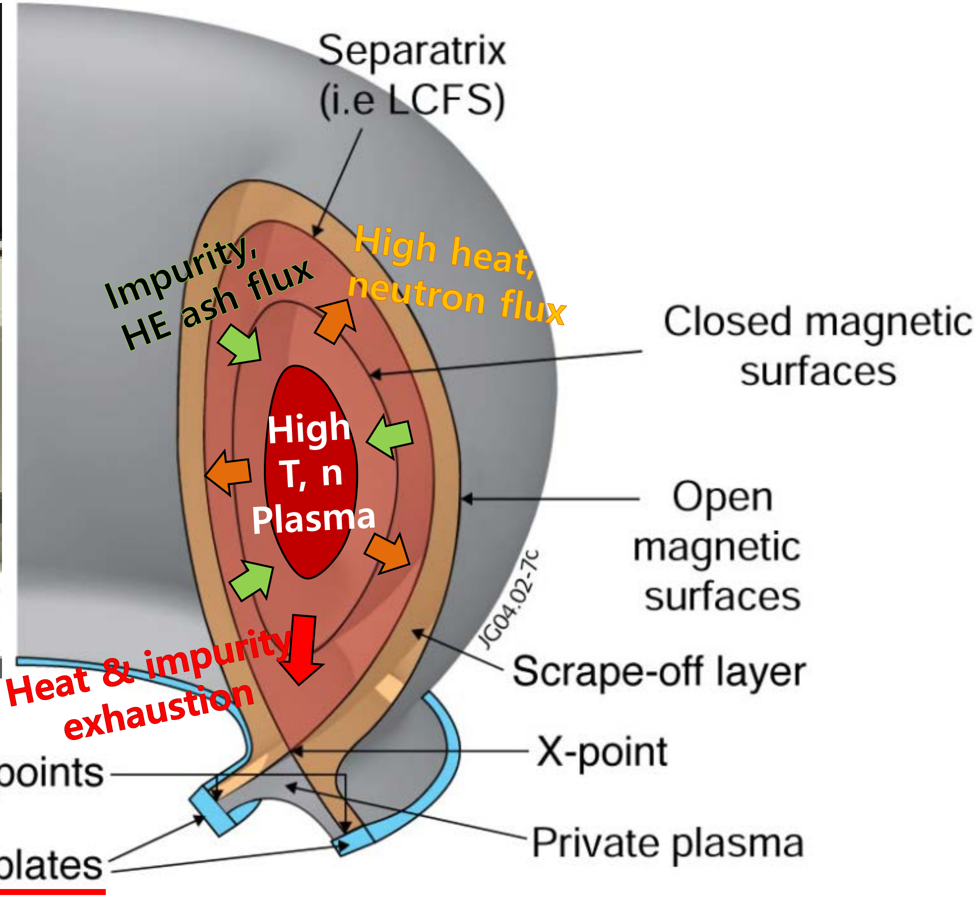
- D + T → He + n + E (17.6MeV)
- Safe and clear energy source
- Infinite energy source

Plasma Facing Components

Plasma Facing Components(PFC) : divertor, first wall



http://www.iter.org/mach/divertor
http://www.efda.org/fusion/focus-on/limiters-and-dive

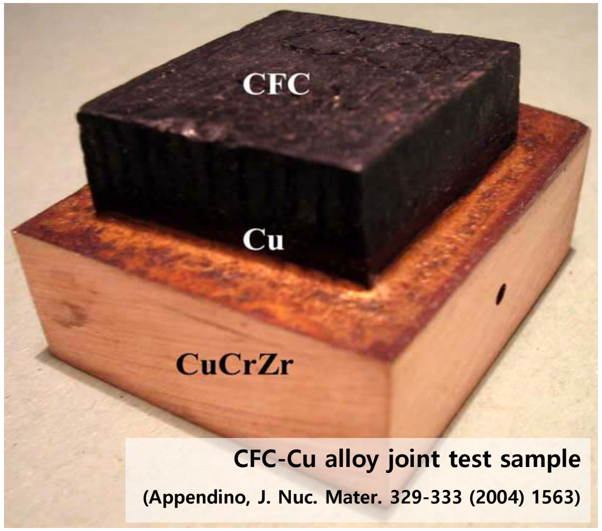


<Requirements>

1) **High Melting Point**
2) **High Plasma & Neutron resistivity**
3) **High Thermal Conductivity**
4) **Low DBTT & good high T strength**

Plasma Facing Components

“Low-Z”
Plasma-facing materials
(Be, CFCs)



CFC-Cu alloy joint test sample

(Appendino, J. Nuc. Mater. 329-333 (2004) 1563)

-High melting point

-High plasma erosion

-High tritium confinement effect

(→ Decrease in efficiency)

“High-Z”
Plasma-facing materials
(W & W alloys)

W “Dome” component for divertor

(http://www.iter.org/newsline/48/645)

-High melting point

-Low plasma erosion

-Low tritium confinement effect

-High DBTT

W alloys are promising for plasma-facing materials

Limitation of pure W as Divertor Materials

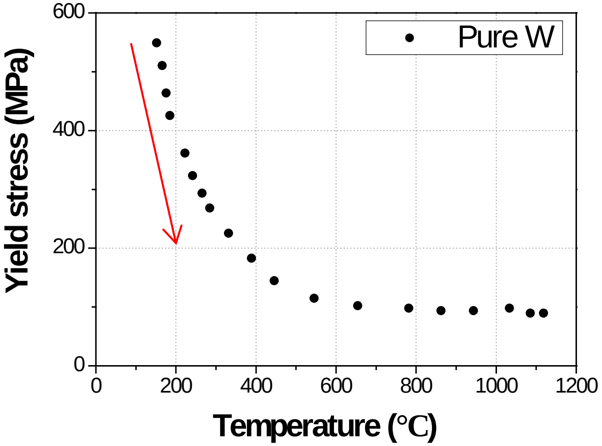
VIB
74
W
183.84

- MP: 3422℃
- Low Deuterium Retention
- Low Ductility (High DBTT: 800℃)

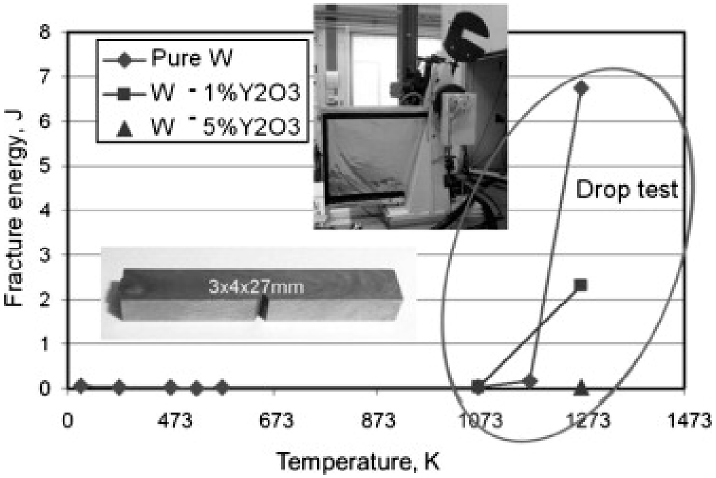
→ DBTT? (Ductile to Brittle Trans. Temp.)

- Characteristics of BCC metal
- Dramatically increased fracture toughness
- Affected by processing, purity, etc..

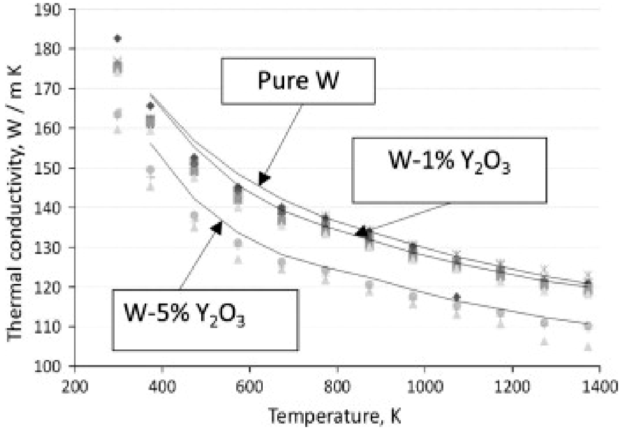
▸ Severe high temperature softening



▸ Poor ductility, High DBTT



▸ Decreasing thermal conductivity at high temperature



D. T. Blagoeva, et. al., Jour. Nucl. Mater., 2013

Methods for improving properties of tungsten

To Improve
Mechanical property

VIB

74

W

183.84

- **MP: 3422℃**
- **Low Deuterium Retention**
- **Low Ductility (High DBTT)**

Methods for controlling extrinsic properties of tungsten

1. Ultra fine grained tungsten

2. Tungsten fiber reinforced tungsten

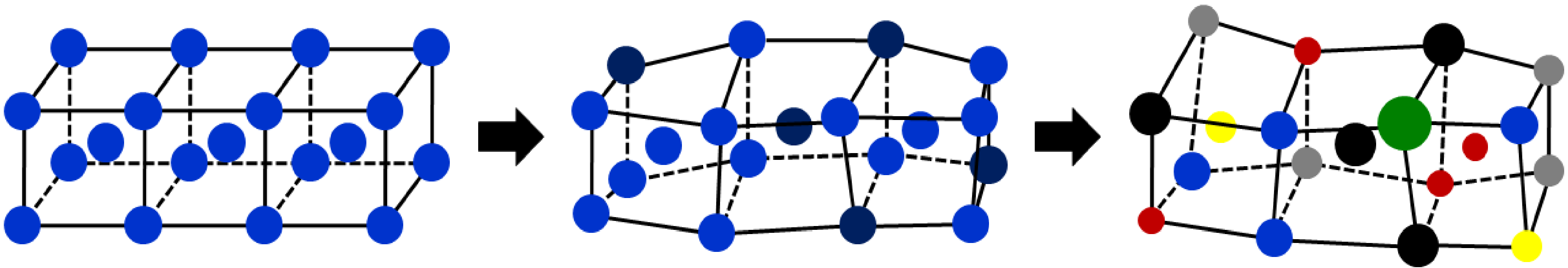
3. Severe plastic deformed tungsten

4. Particle dispersed tungsten (ODS, CDS…)

- **Methods for controlling extrinsic property of tungsten could not change tungsten's original brittle nature.**

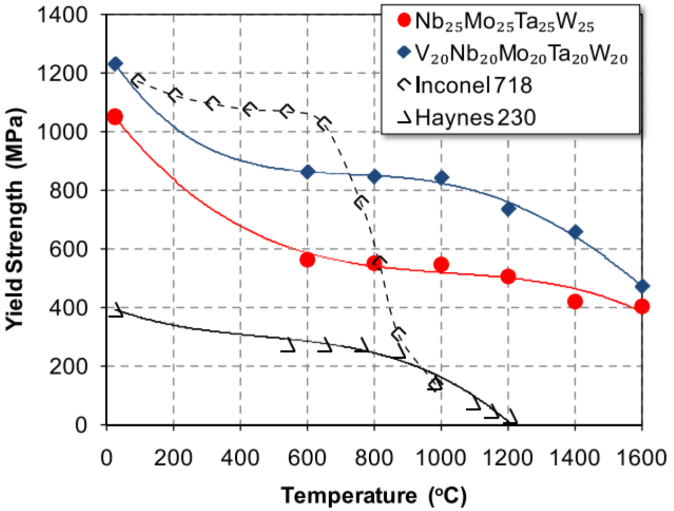
→ Research of controlling tungsten's <u>intrinsic nature</u> is needed

High Entropy Alloy Concept for Changing Intrinsic Property



Yun Jun Zhou et al., (2008)

Tungsten, W → **W-TM solid solutions** → **W-TM$_1$-TM$_2$-TM$_3$-TM$_4$ HEA**

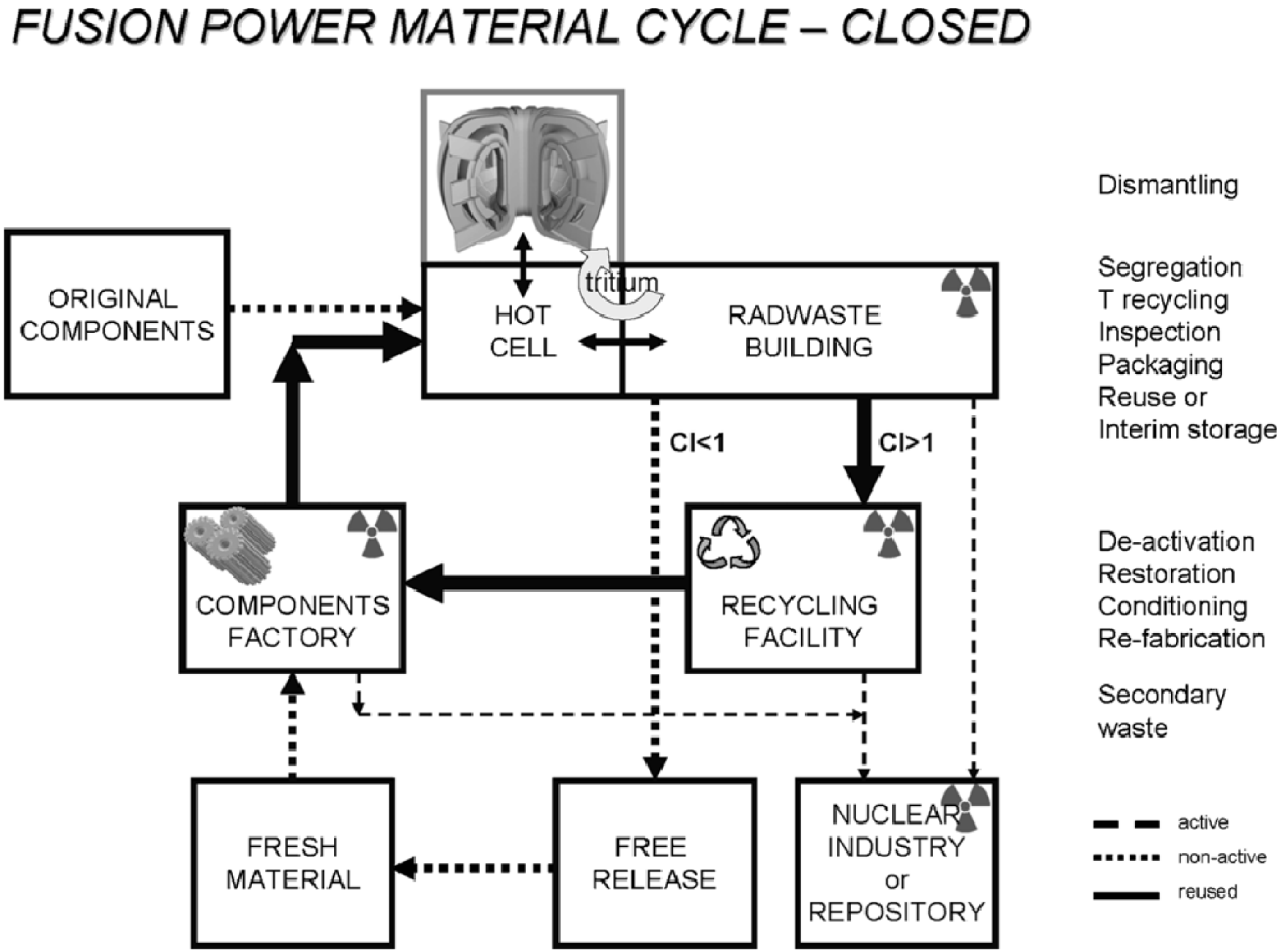


O.N. Senkov et al., *Intermetallics*, 2011

Features of refractory high-entropy alloys

- Maintaining high yielding stability until high temperature
- Although V had lower T_m compared with other elements, yield strength increased.
- Reduced DBTT (~600℃) compared to W (~1000℃)
- Nb, Mo is restricted to few ppm in fusion reactor. (high activation elements)

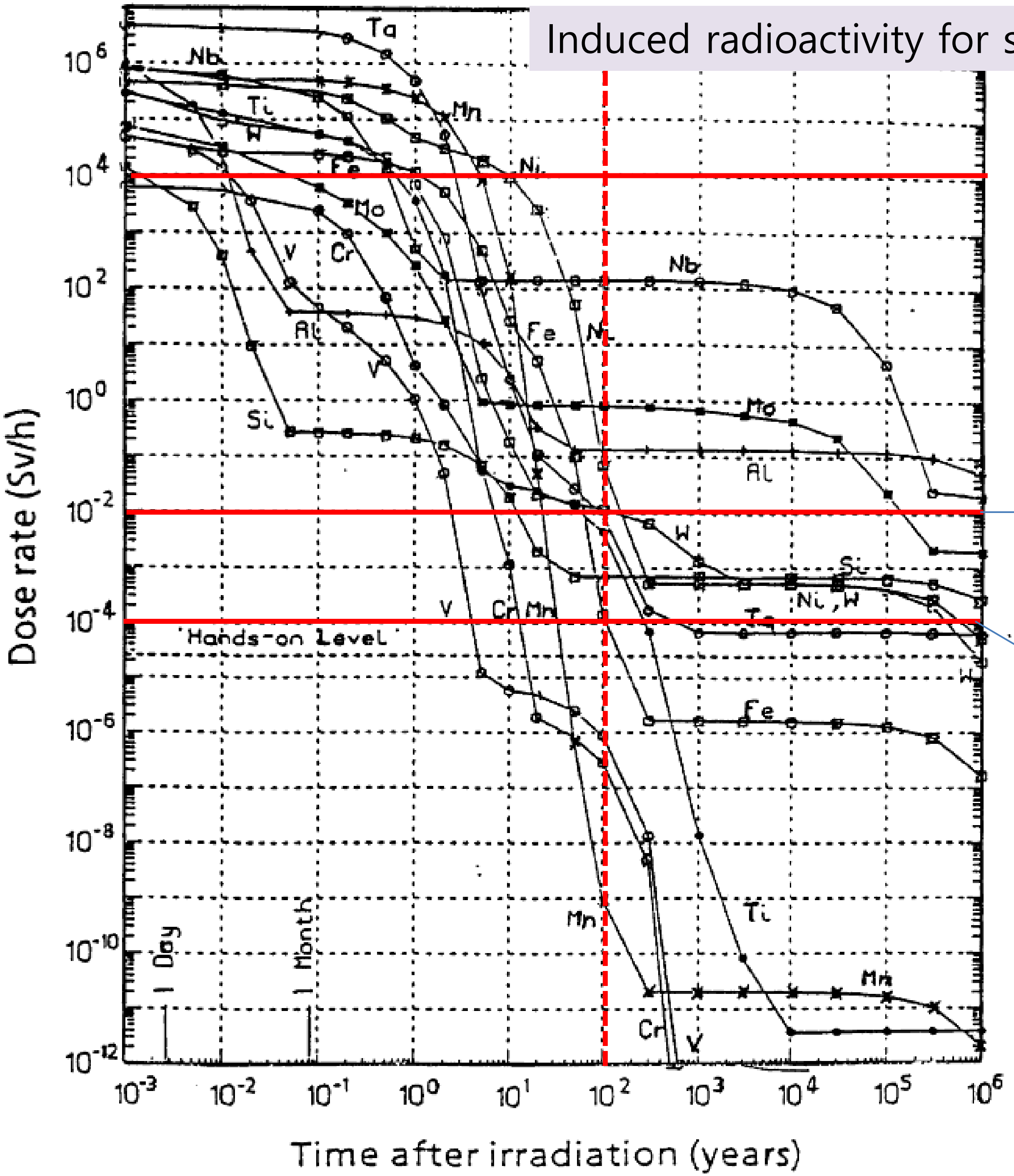
Low Activation Elements – Remote Handling Concept of Fusion Reactor



<Requirements>

1) Dose rate ↑
2) Decay heat ↓

Induced radioactivity for selected elements



Recycling limit (conservative)

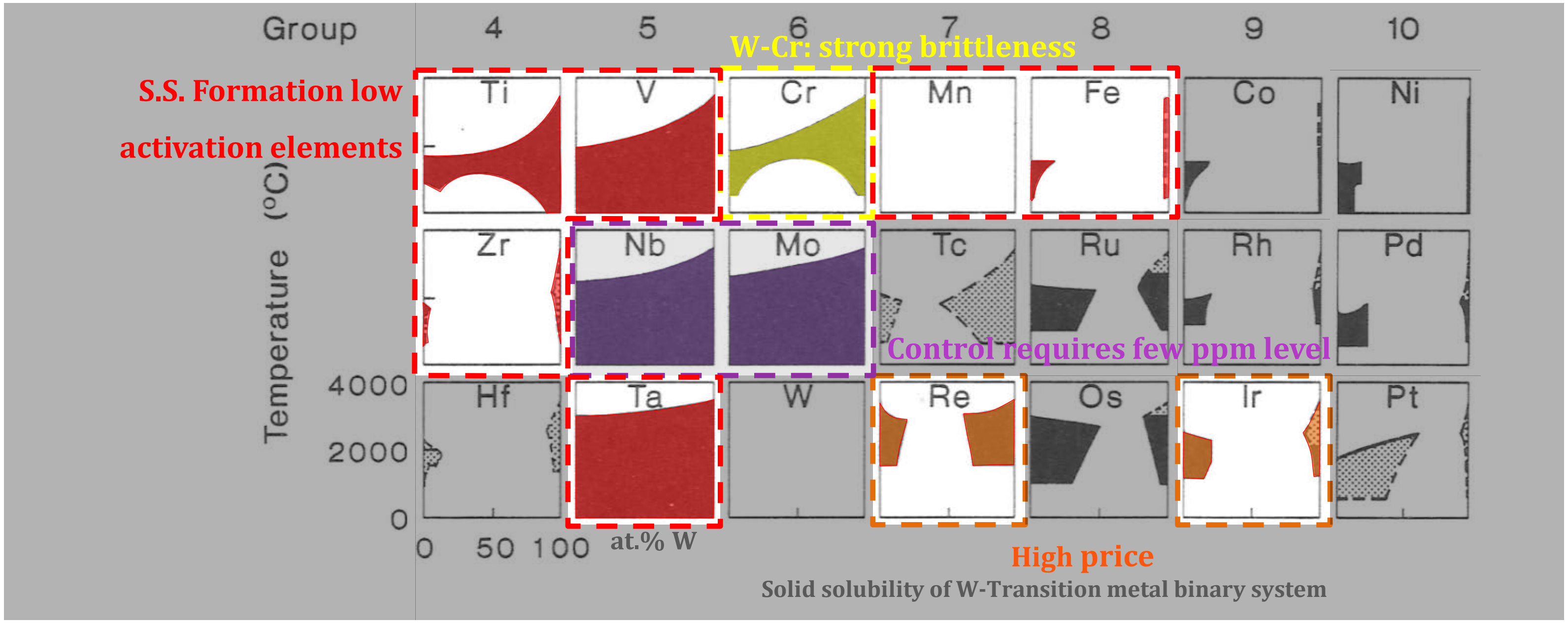
Nb, Mo, Al, Ni x

Hands-on limit

Using Low Activation Elements!

Elements Selection for W-based solid solution alloys

Solid solubility of W-TM binary system

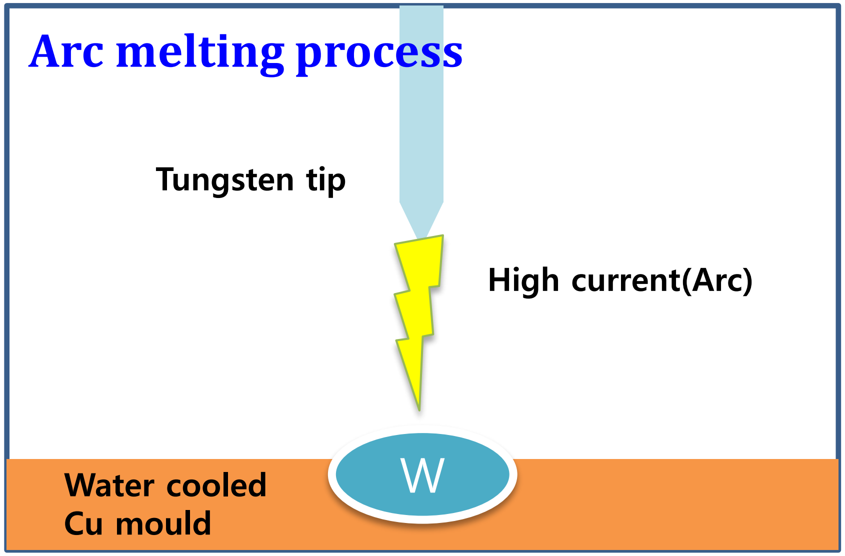


Solid solubility of W-Transition metal binary system

1) **Low activation elements**
2) **High solubility with W**

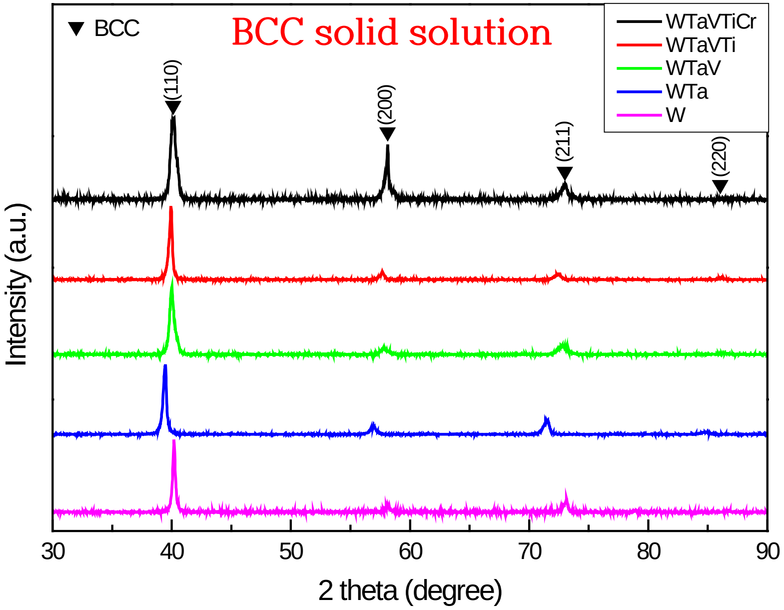
→ **Ti, V, Cr, Ta**

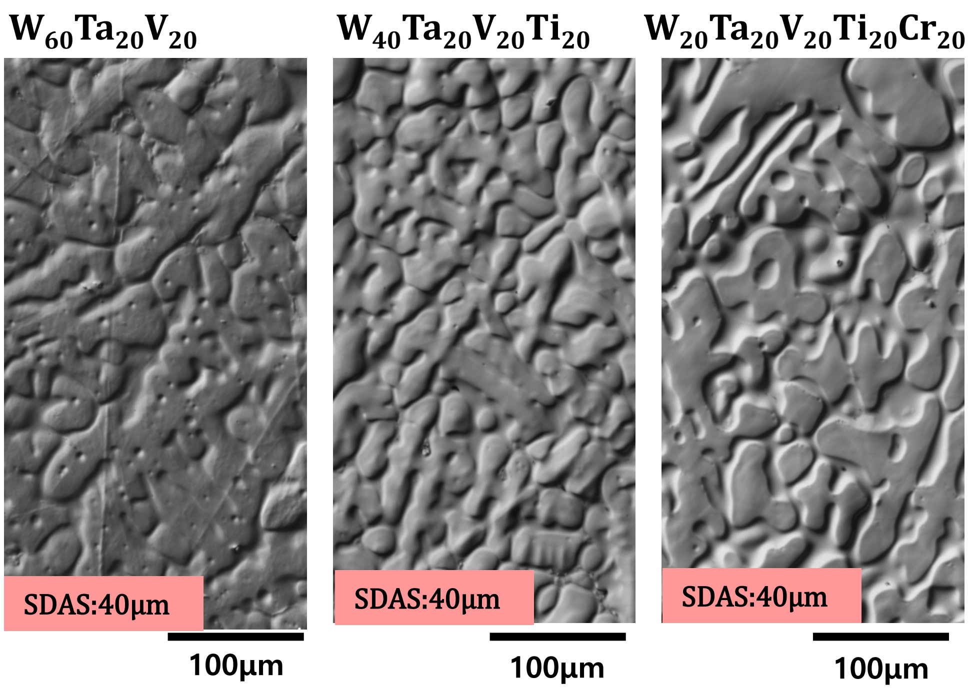
Elements	Melting (℃)	Boiling (℃)
W	**3410**	5700
Ta	**2996**	5427
V	1900	**3407**
Ti	1668	**3260**
Cr	1875	**2680**



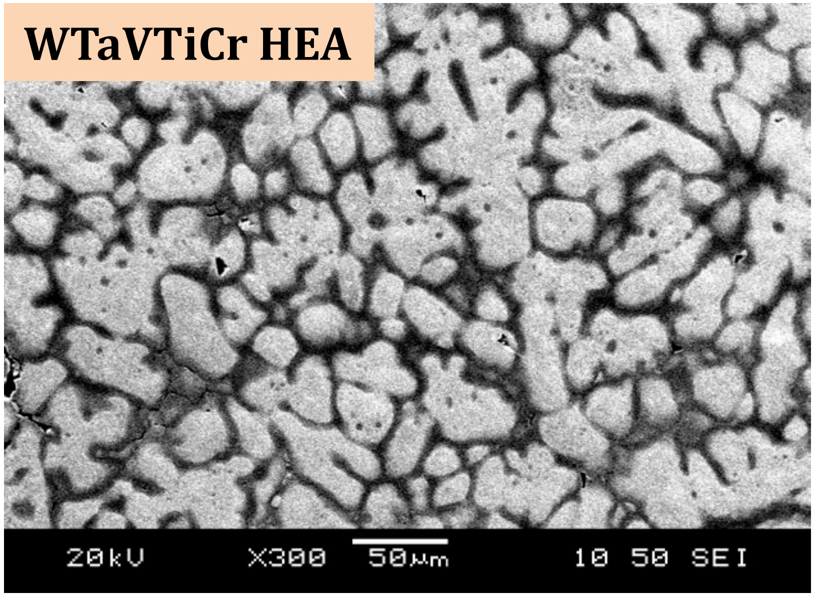
Arc melting process

Characterization of W-based Multicomponent Alloys





Dendrite structure



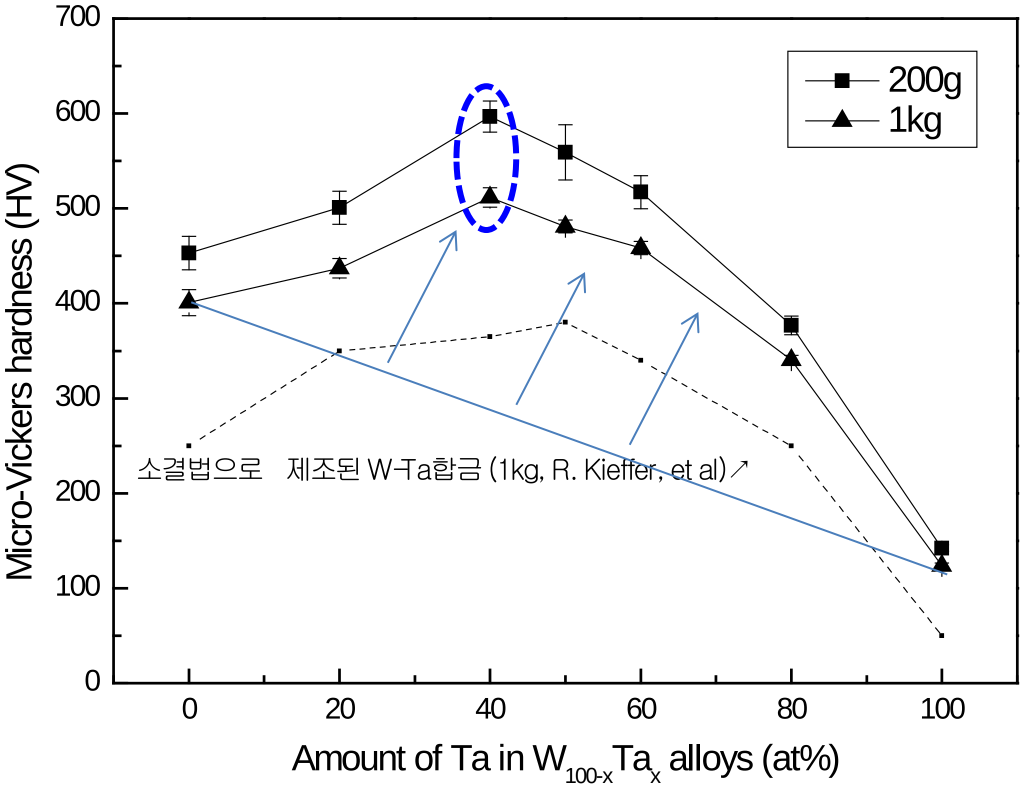
EDS composition analysis (at. %)

	W	Ta	V	Ti	Cr
WTaVTiCr	18.14	18.64	23.94	20.8	20.68
WTaVTi	40.16	21.08	20.25	18.51	0
WTaV	59.75	20.07	20.19	0	0

2. Mechanical properties:

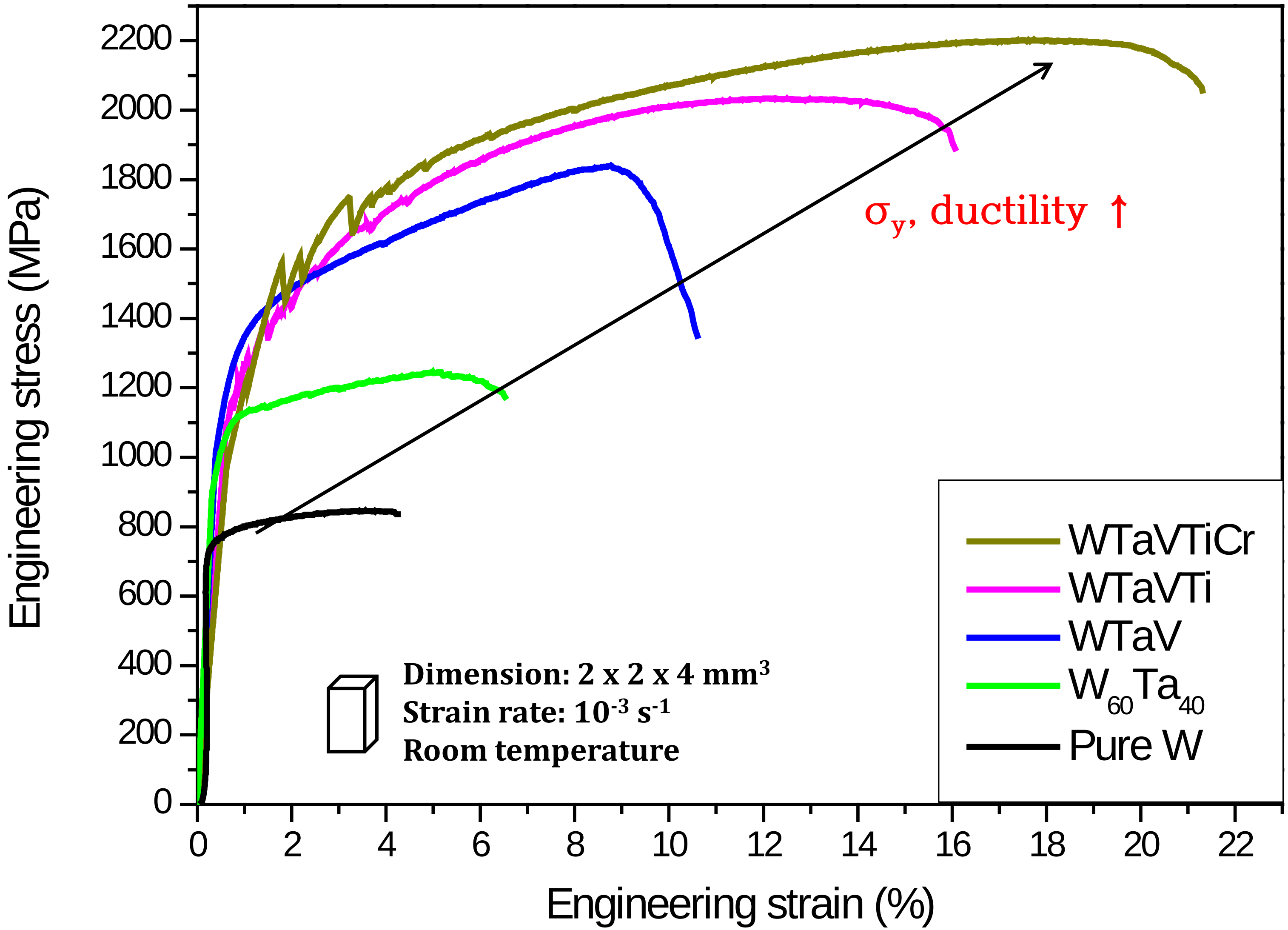
High Temperature Compressive Tests

Hardness Results of W-Ta binary alloy



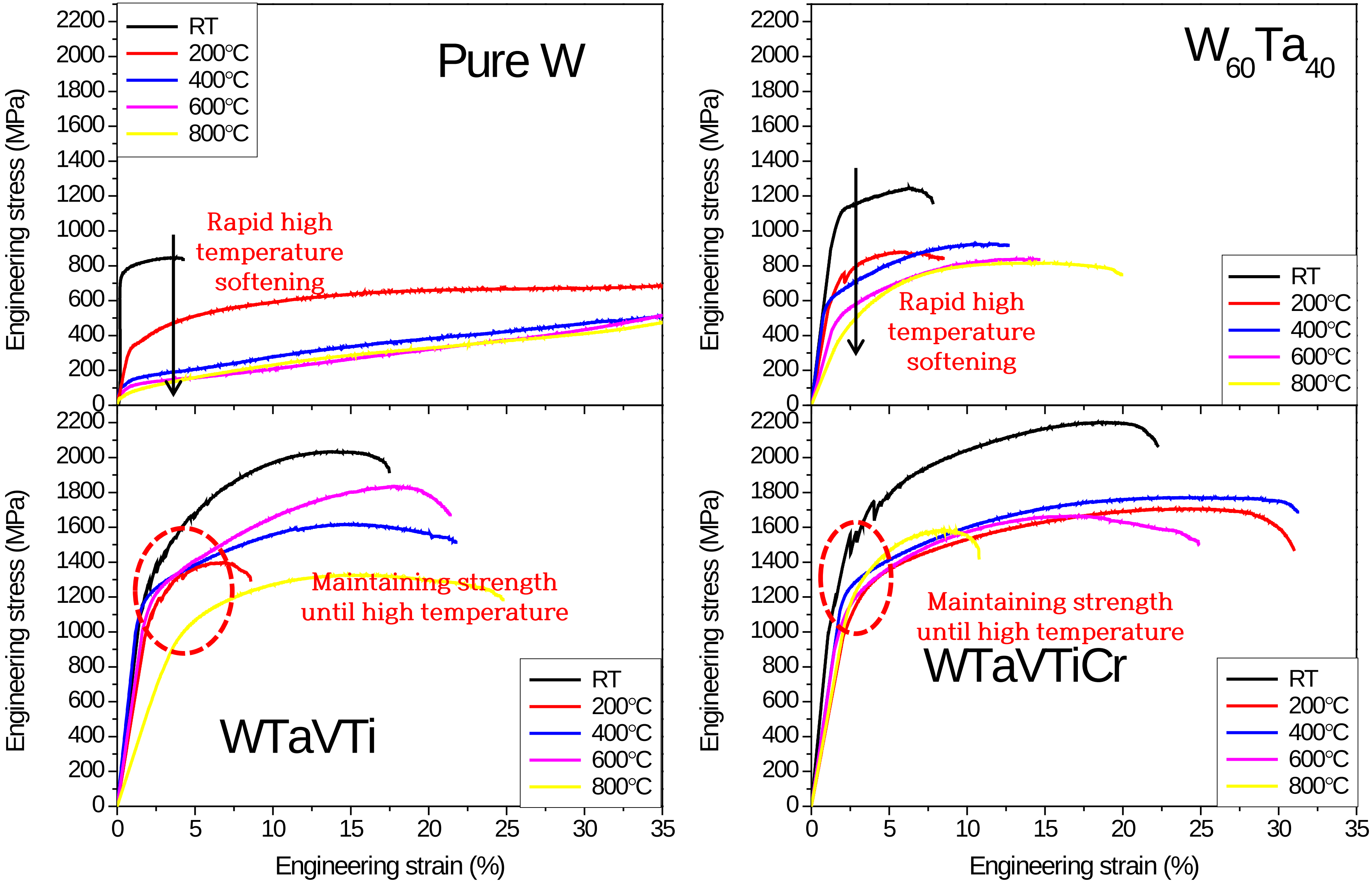
- Higher hardness than sintered sample
- Affected by solid solution hardening

Results of Room Temperature Compression Tests



- **Unary to Quinary : Yield strength and elongation increased!**

Results of Compression Tests at Various Temperatures (up to 800℃)



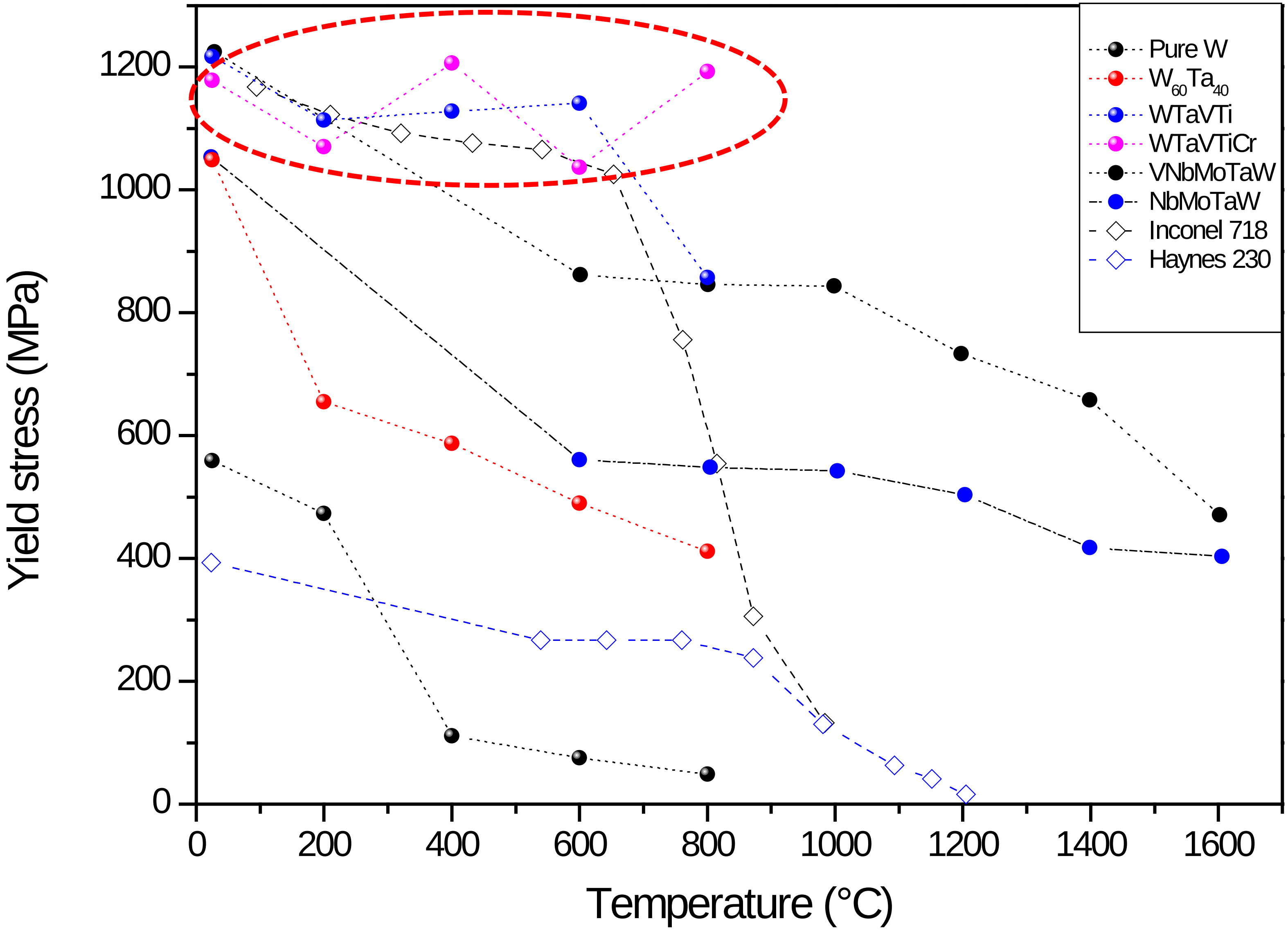
Rapid high temperature softening

Rapid high temperature softening

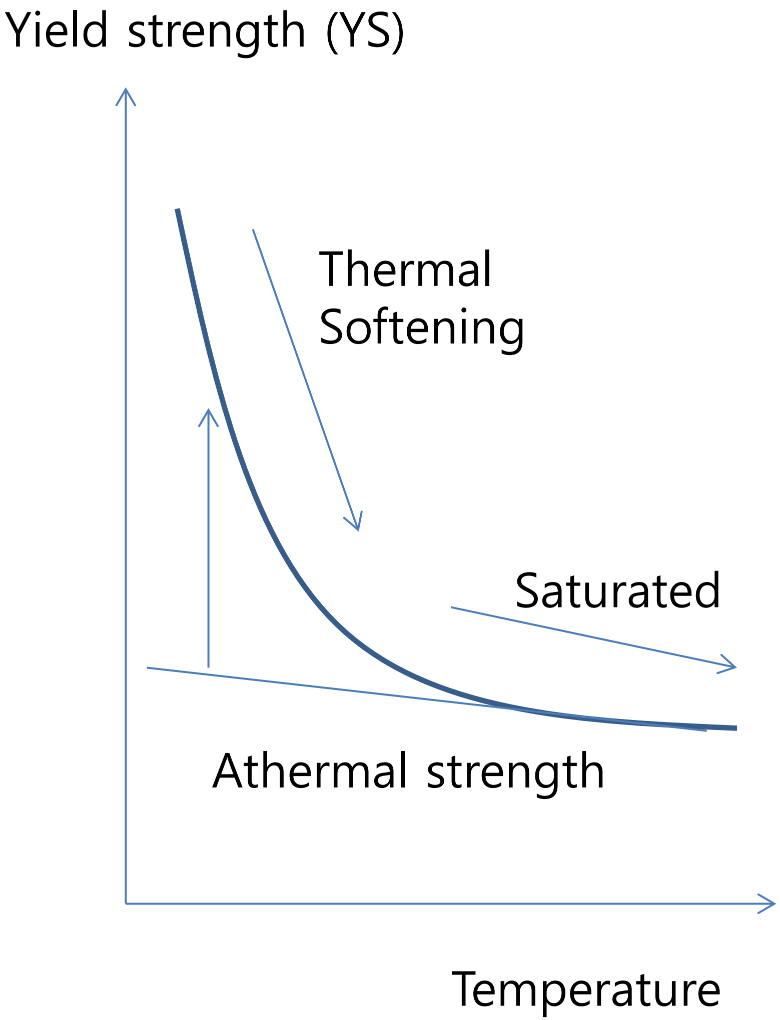
Maintaining strength until high temperature

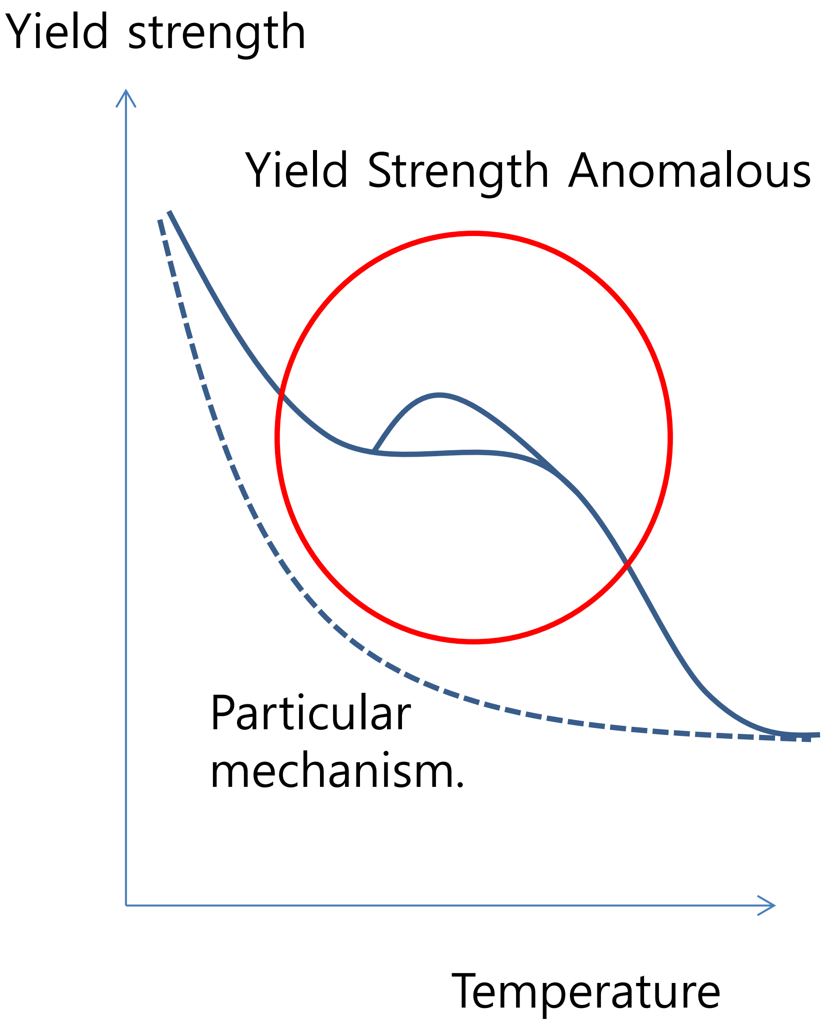
Maintaining strength until high temperature

YS comparison with various high temp. materials (up to 800℃)



Discussion: Yield Strength Anomalous

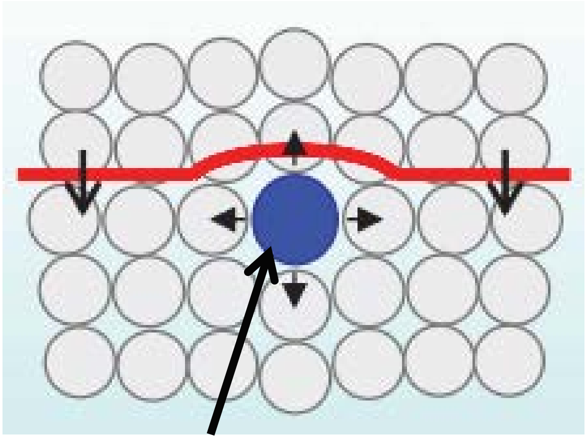




For Hardening
1) Athermal strength ↑
2) Inducing yield strength anomalous

Hardening Mechanism in Alloys

1. Solid Solution Hardening

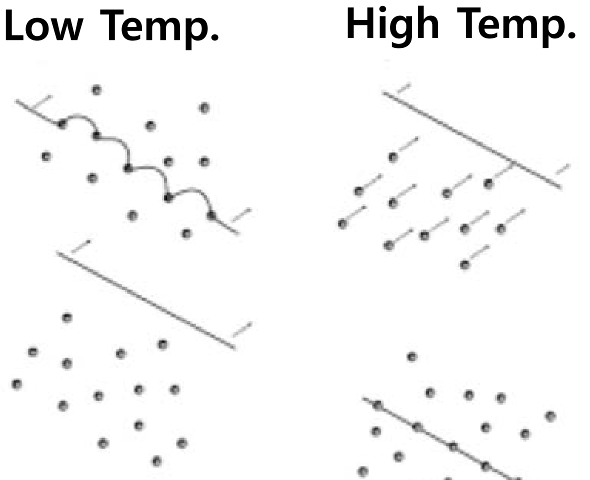


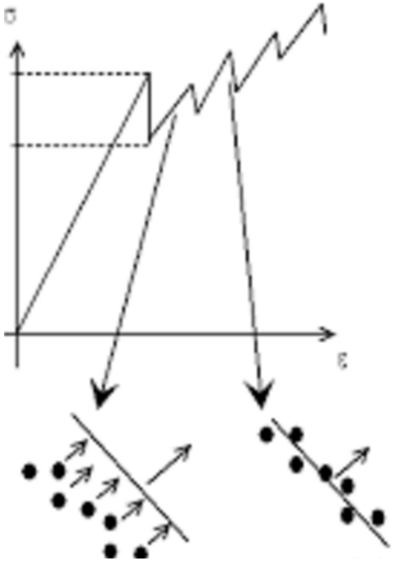
K. Lu et al. (2009)

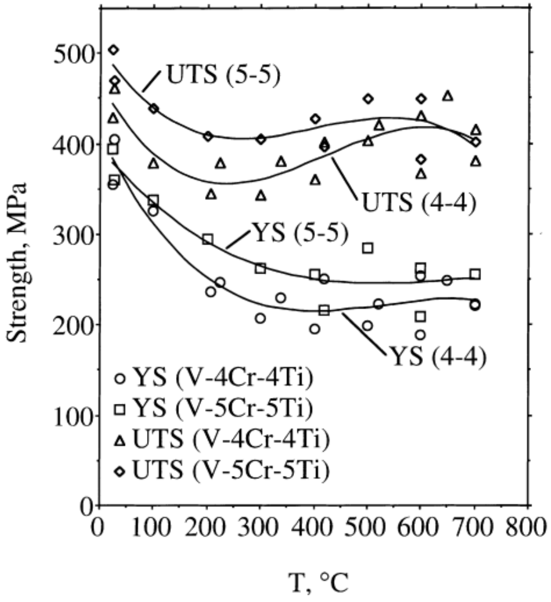
Atomic size mismatch parameter, $\boldsymbol{\varepsilon}_{\mathrm{a}}$

$$\therefore \boldsymbol{\varepsilon_a = (1/a)(da/dc)}$$

2. Dynamic Strain Aging (Mechanism of Portevin Le-Chatelier effect)



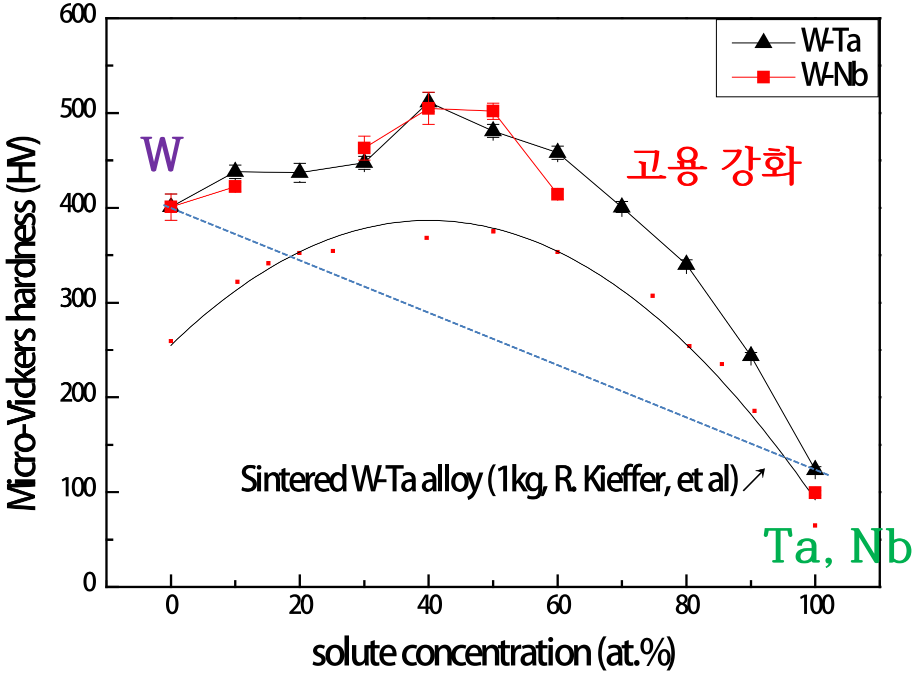




Solid Solution Hardening Factor

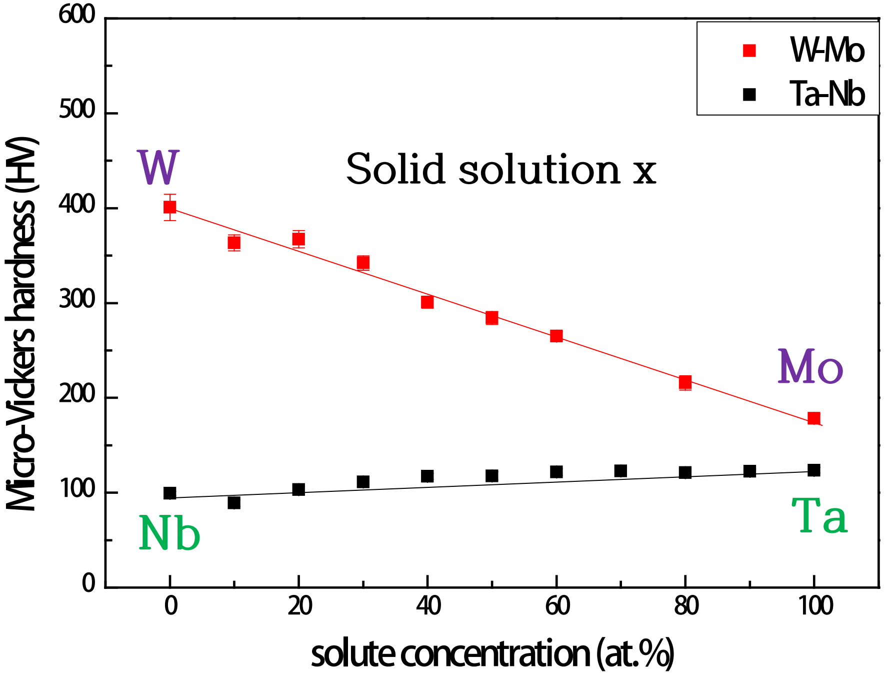
W-Ta/ W-Nb alloy

-6 kJ/mol -8 kJ/mol



W-Mo, Ta-Nb alloy

0 kJ/mol 0 kJ/mol

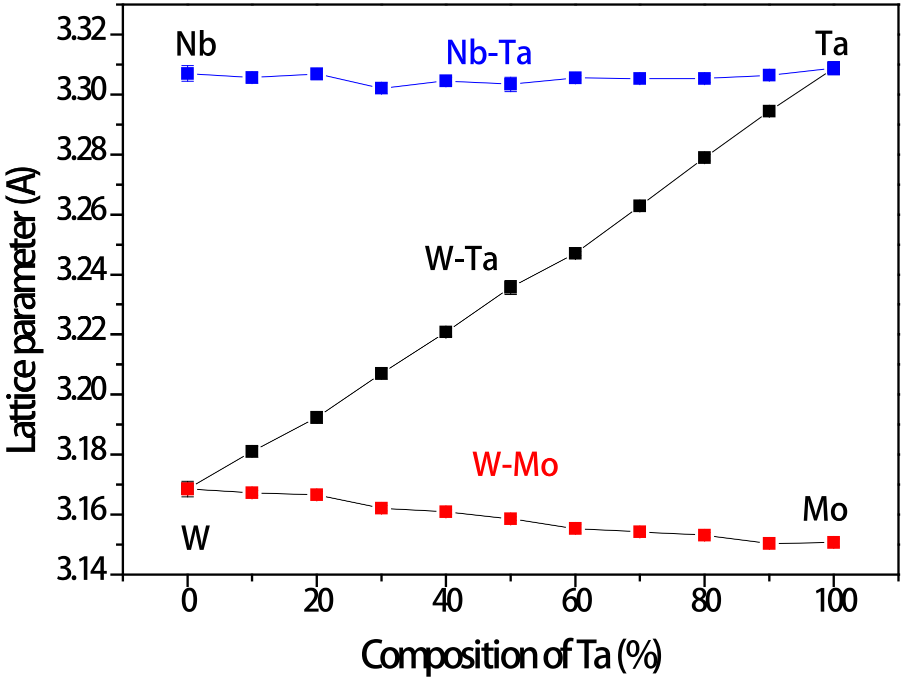


Elements	**W**	**Ta**	**Mo**	**Nb**
Atom size (pm)	**139**	**146**	**139**	**146**

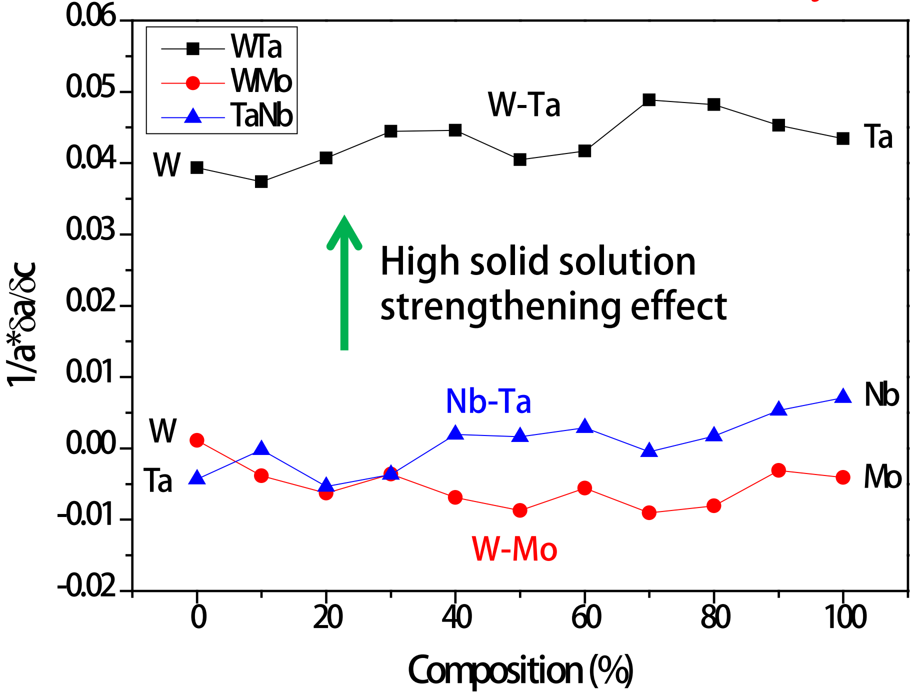
Hardening effect by atomic size mismatch

W–Ta, W–Mo, Ta–Nb

a. Atomic size parameter



b. Atomic size mismatch, δ_i

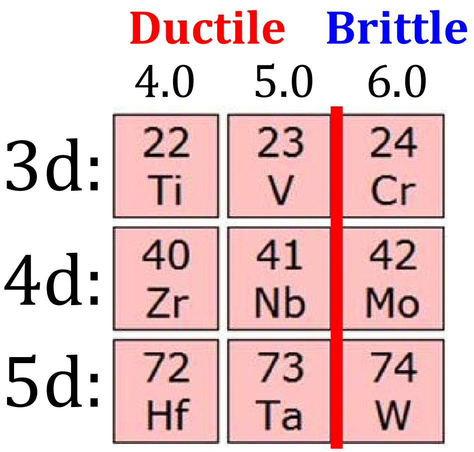


- Atomic size mismatch $\delta_i = \frac{1}{a}\frac{\partial a}{\partial c}$ (a: lattice parameter, c: concentration)
- Hardening is induced by difference of atom size

Elements	**W**	**Ta**	**V**	**Ti**	**Cr**
Atom size (pm)	**139**	**146**	**134**	**147**	**128**

Factor of Ductility in BCC alloy

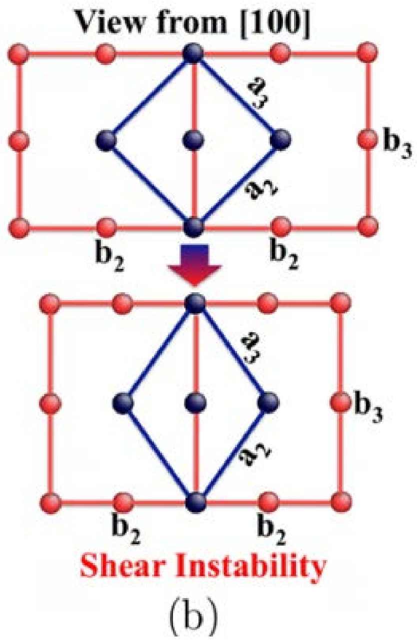
Valence electron configuration (VEC)

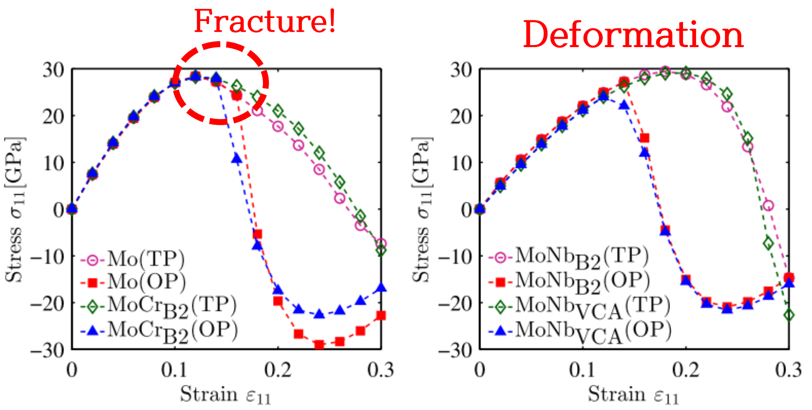


Ductile **Brittle**

	4.0	5.0	6.0
3d:	22 Ti	23 V	24 Cr
4d:	40 Zr	41 Nb	42 Mo
5d:	72 Hf	73 Ta	74 W

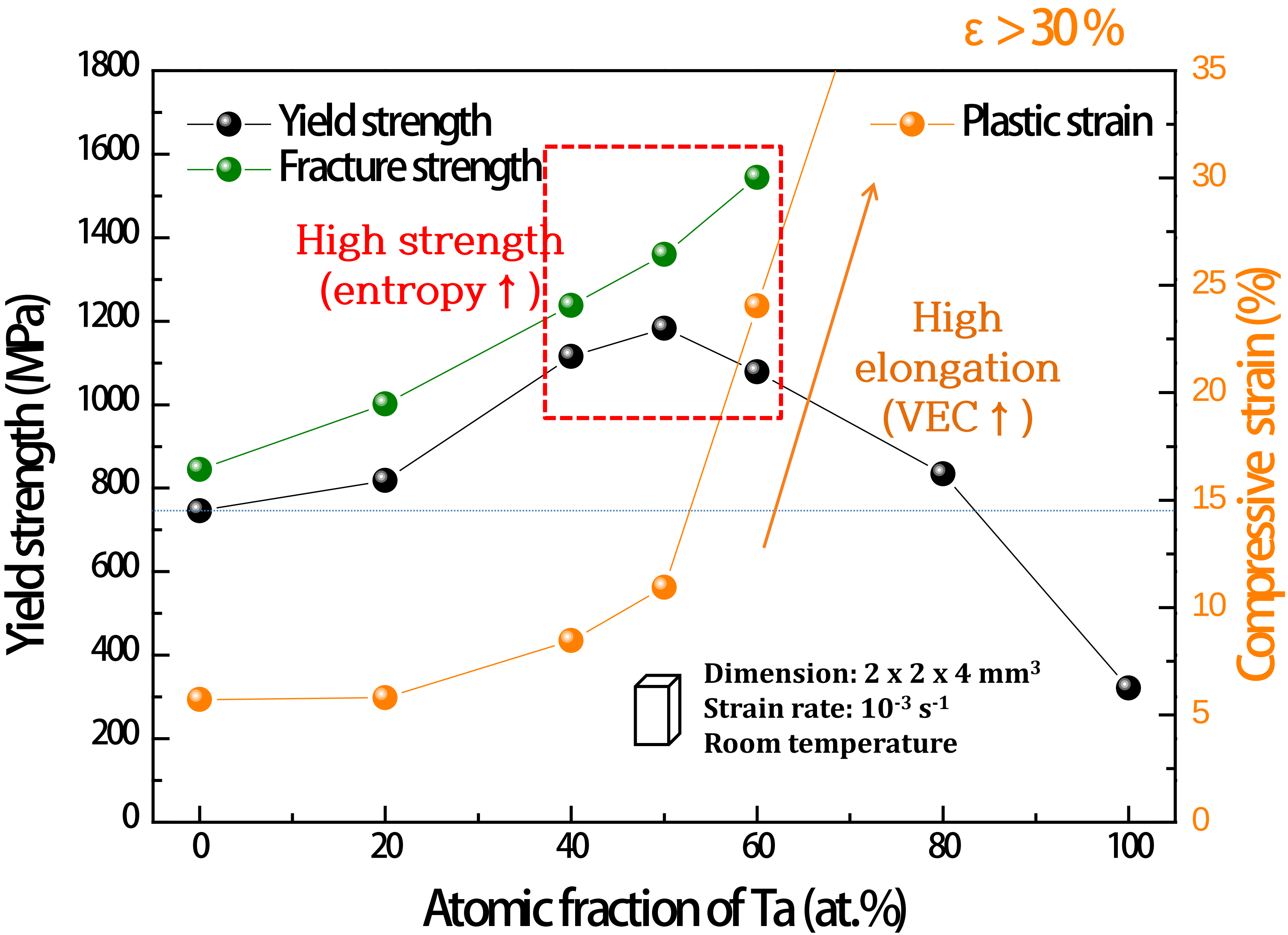
- **Relating to ductility**
- **Easily manipulated by compositional change**
- **Ta, Ti, V can be promising elements for decreasing VEC**
- **Shear instability (intrinsically ductile) ↑**



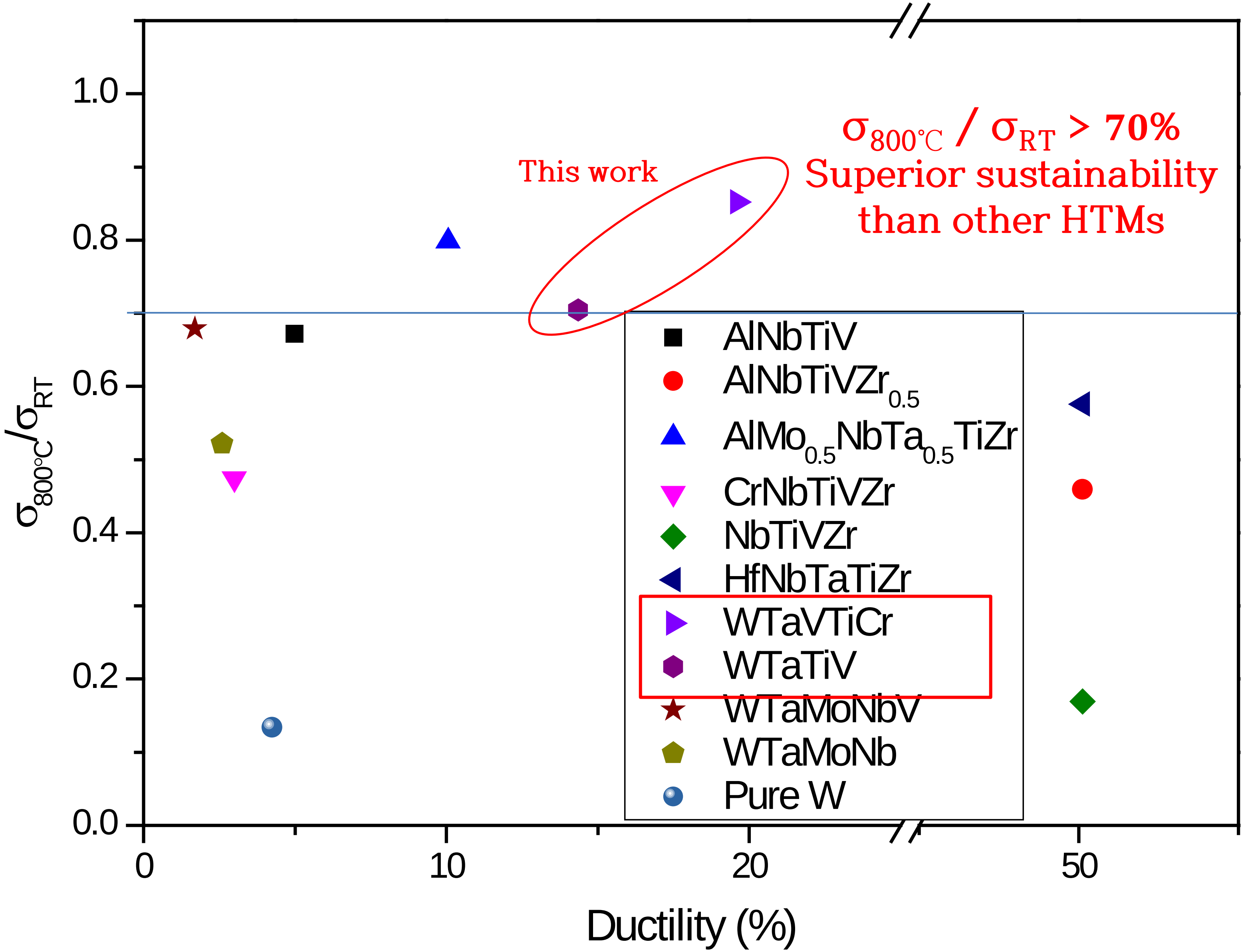


Qi, Liang, et al., *PRL*, 2014

Results of Compression test of W-Ta binary alloy



Comparison of YS reduction and ductility with various HTMs



This work

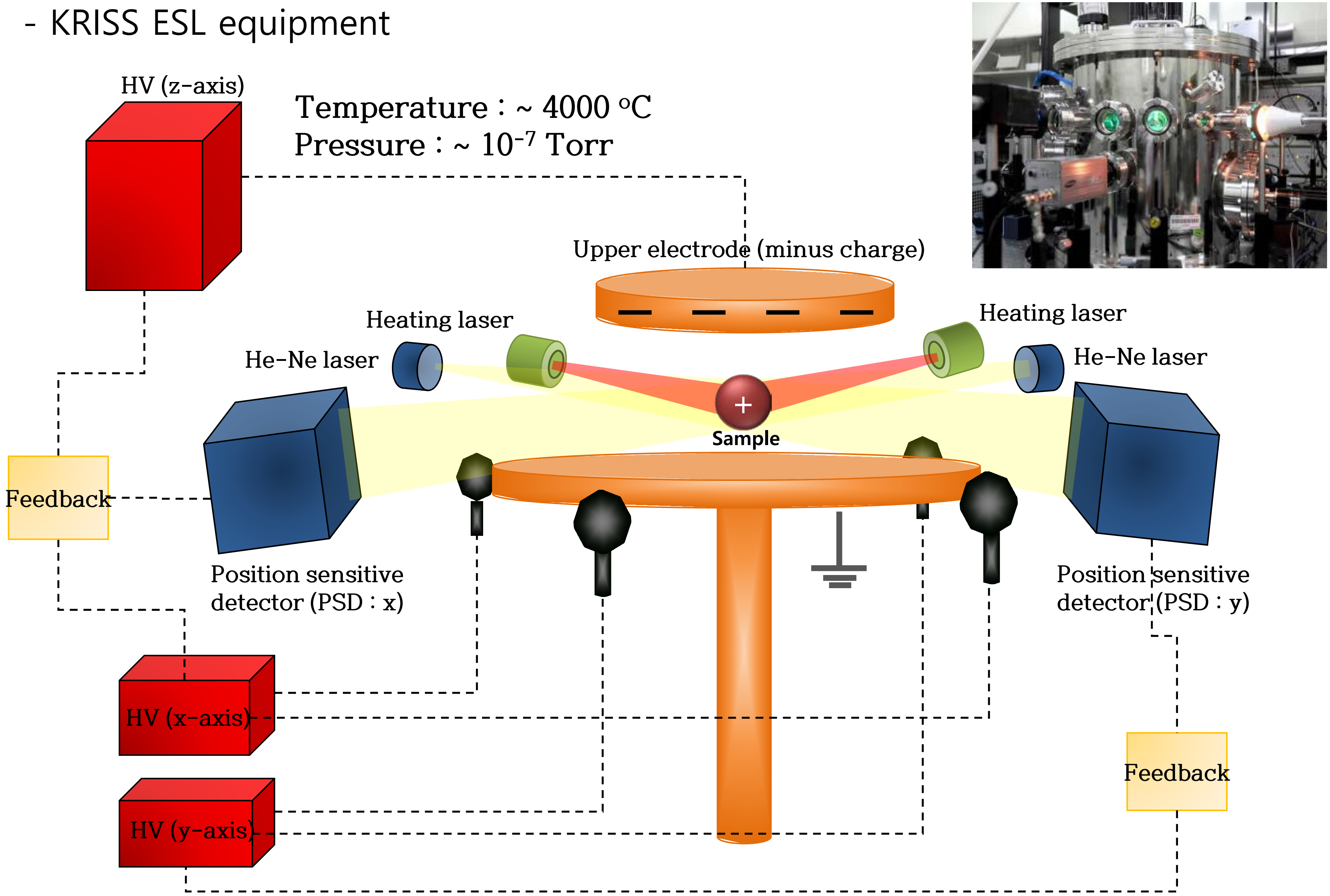
$\sigma_{800℃} / \sigma_{RT} > 70\%$

Superior sustainability than other HTMs

3. Thermal properties:
Electrostatic Levitation & Thermal Conductivity

Electrostatic Levitation : measurement of T_m and ΔT_N

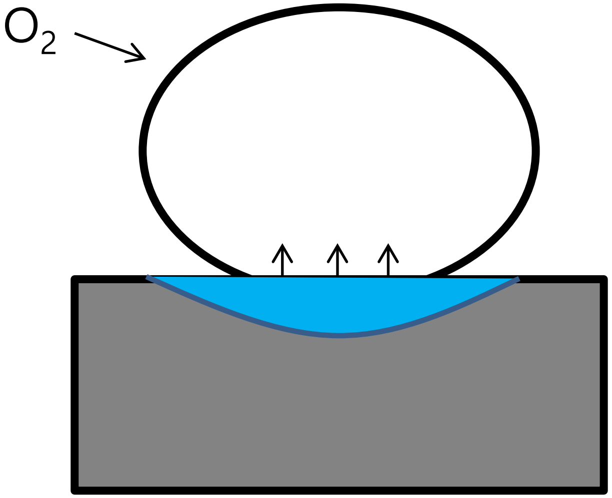
- KRISS ESL equipment



Temperature : ~ 4000 °C
Pressure : ~ 10^{-7} Torr

Electrostatic Levitation : measurement of T_m and ΔT_N

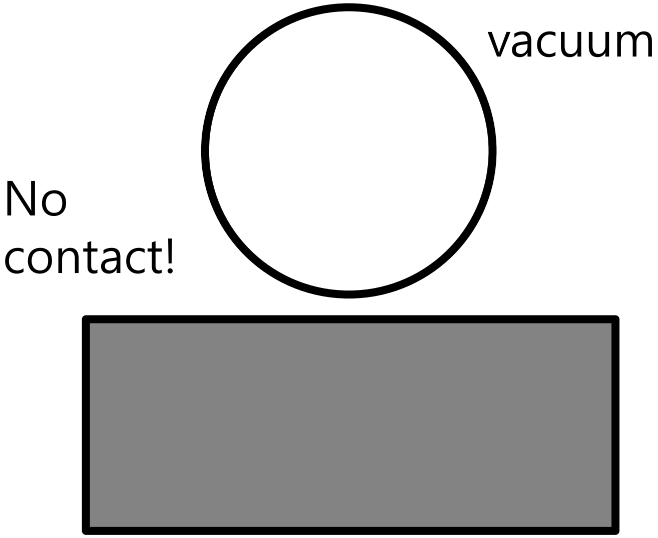
- Contact with container for high temperature measurement

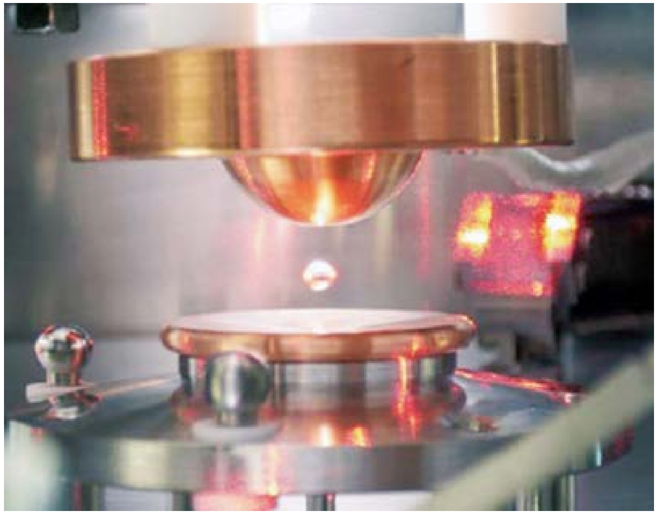


Problems…

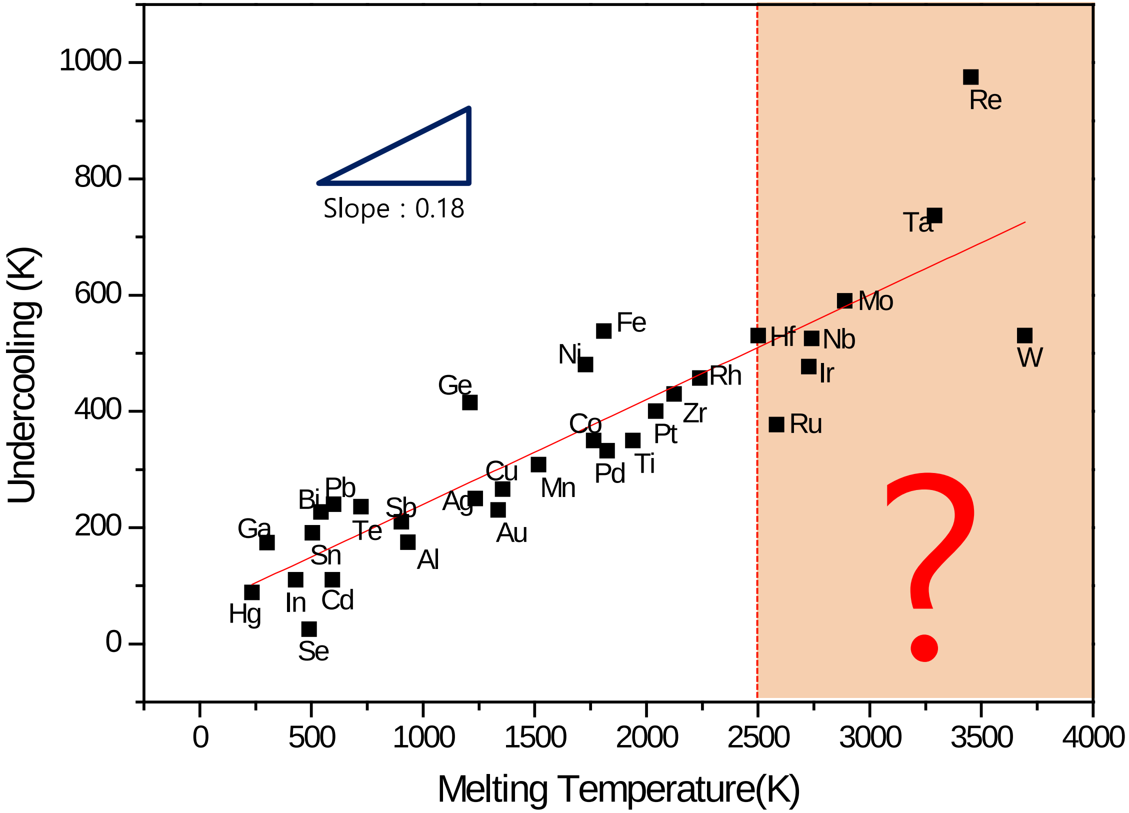
- Contamination
- Container melting
- Oxidation
- Difficult to increase temperature

- Contactless method for high temperature measurement



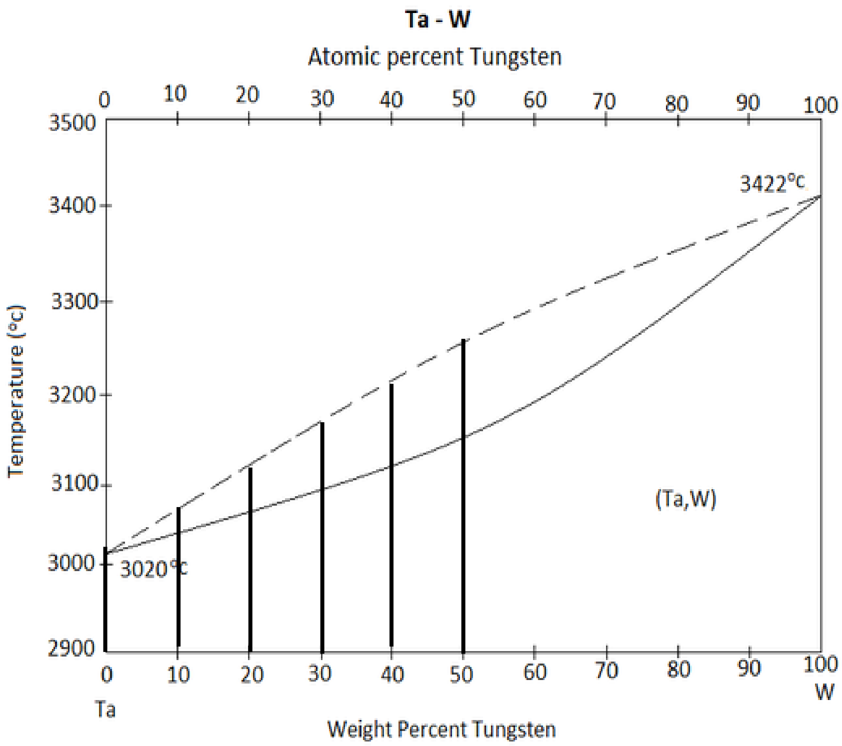


Maximum undercooling study for pure elements



- Undercooling is important for study of phase transformation
- Undercooling increases as melting temperature
- Refractory metals have its melting point >2200℃
- Few results published of high temperature alloys

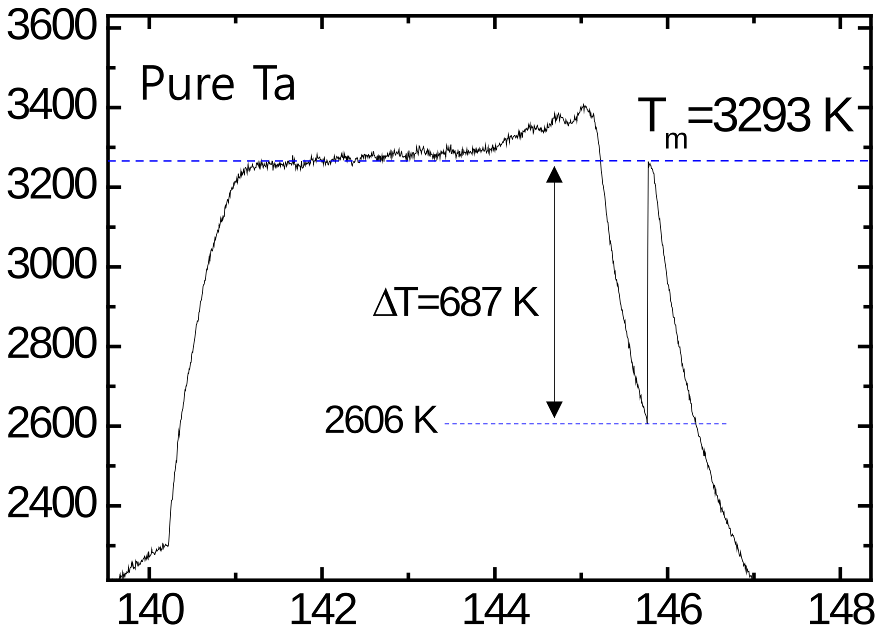
Measurement of maximum undercooling (ΔT_N)by ESL

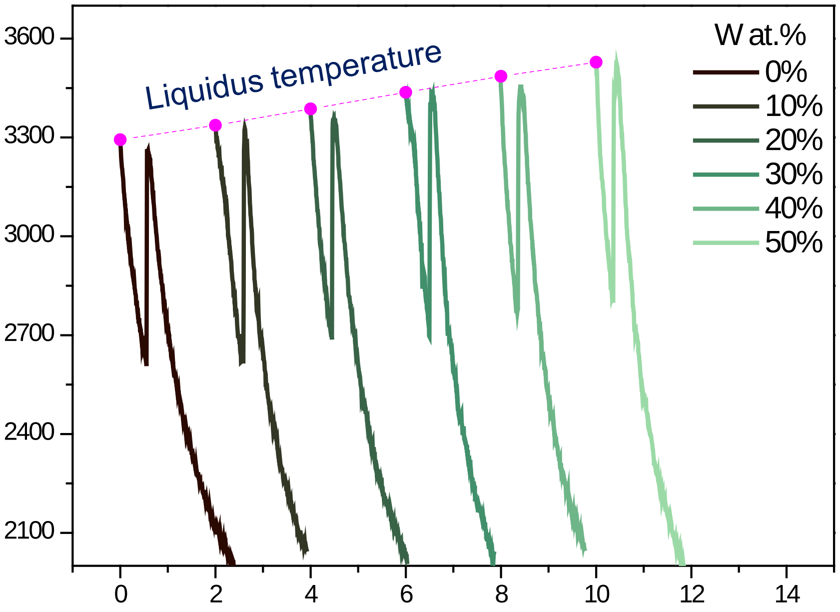


$W_{10}Ta_{90}$ alloy - Recalescence

- **$W_{100\text{-}x}Ta_x$ (x=0,10,20,30,40,50)**
- **W-Ta alloys exhibit high melting temperature above 3000℃**
- **Measuring cooling curves**

Measurement of maximum undercooling (ΔT_N)by ESL

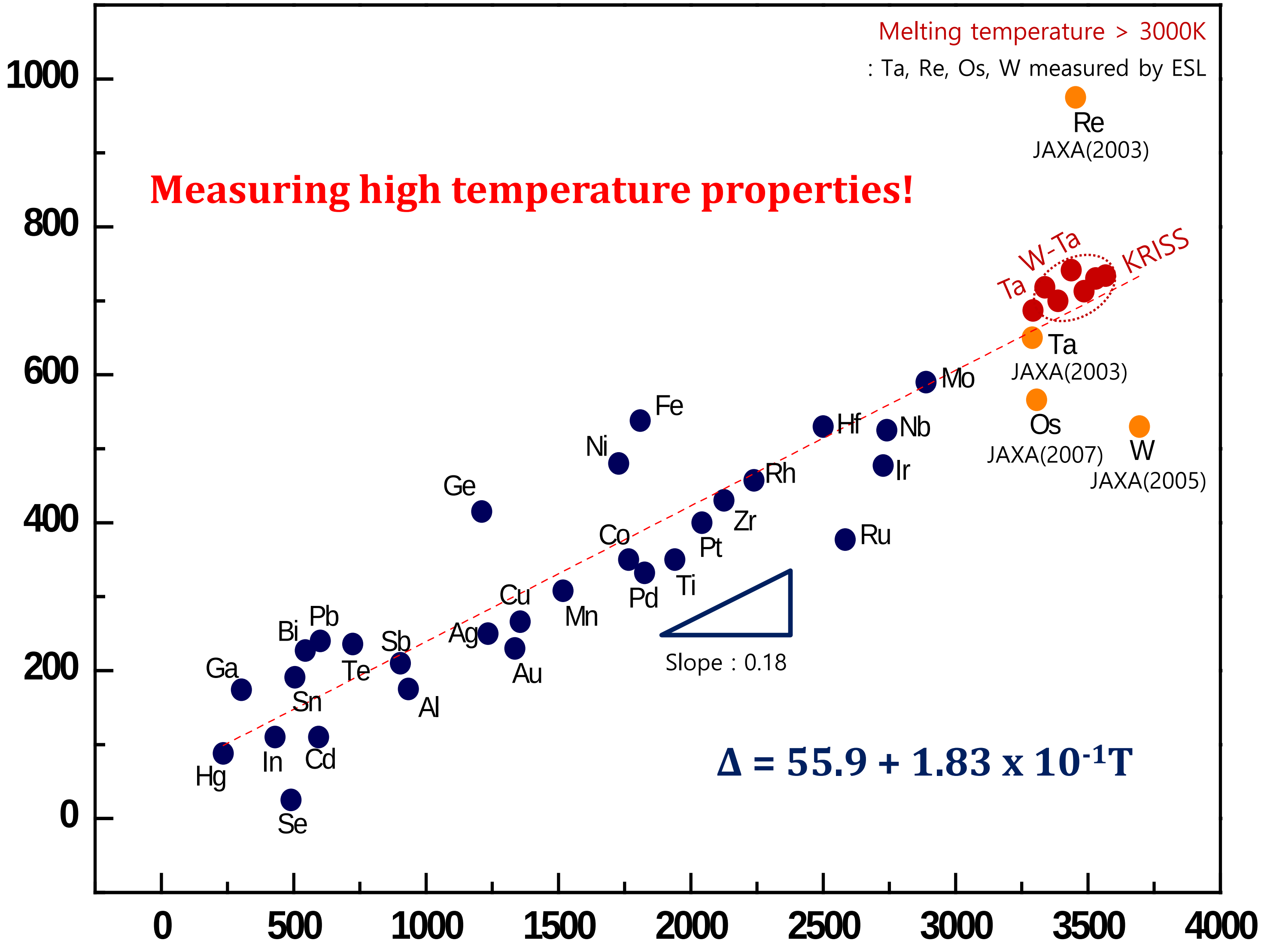




- **Ta-rich W-Ta binary alloy exhibit deep undercooling (~700K)**
- **Plateau region was shorter than low melting elements (~0.1s)**

W contents (at.%)	Undercooling (K)
0	687
10	718
20	700
30	741
40	713
50	730

Maximum undercooling vs. Melting temperature



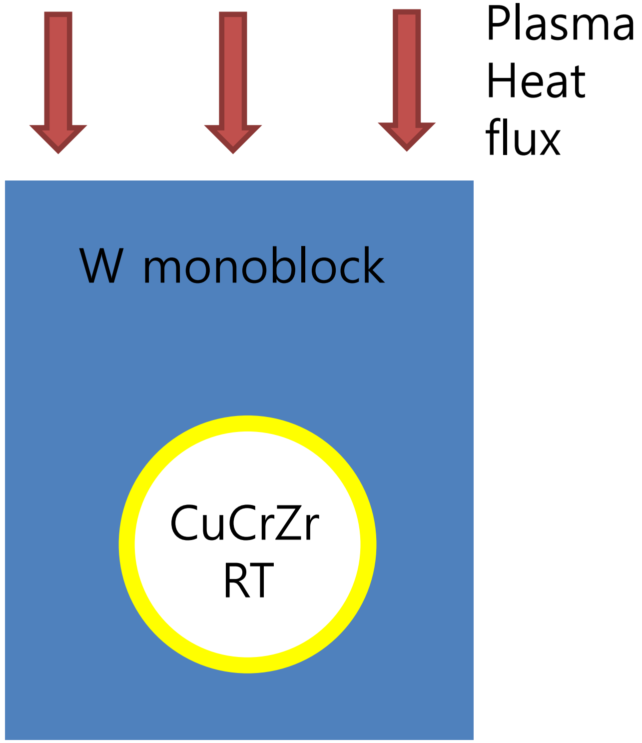
Melting temperature > 3000K

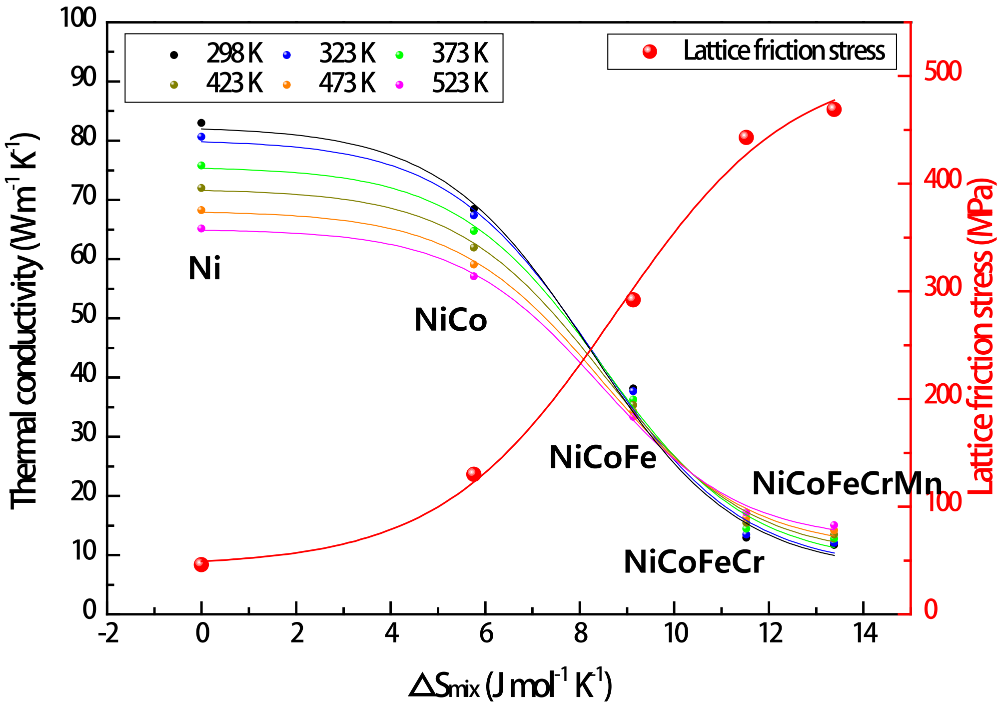
: Ta, Re, Os, W measured by ESL

Measuring high temperature properties!

$$\Delta = 55.9 + 1.83 \times 10^{-1}T$$

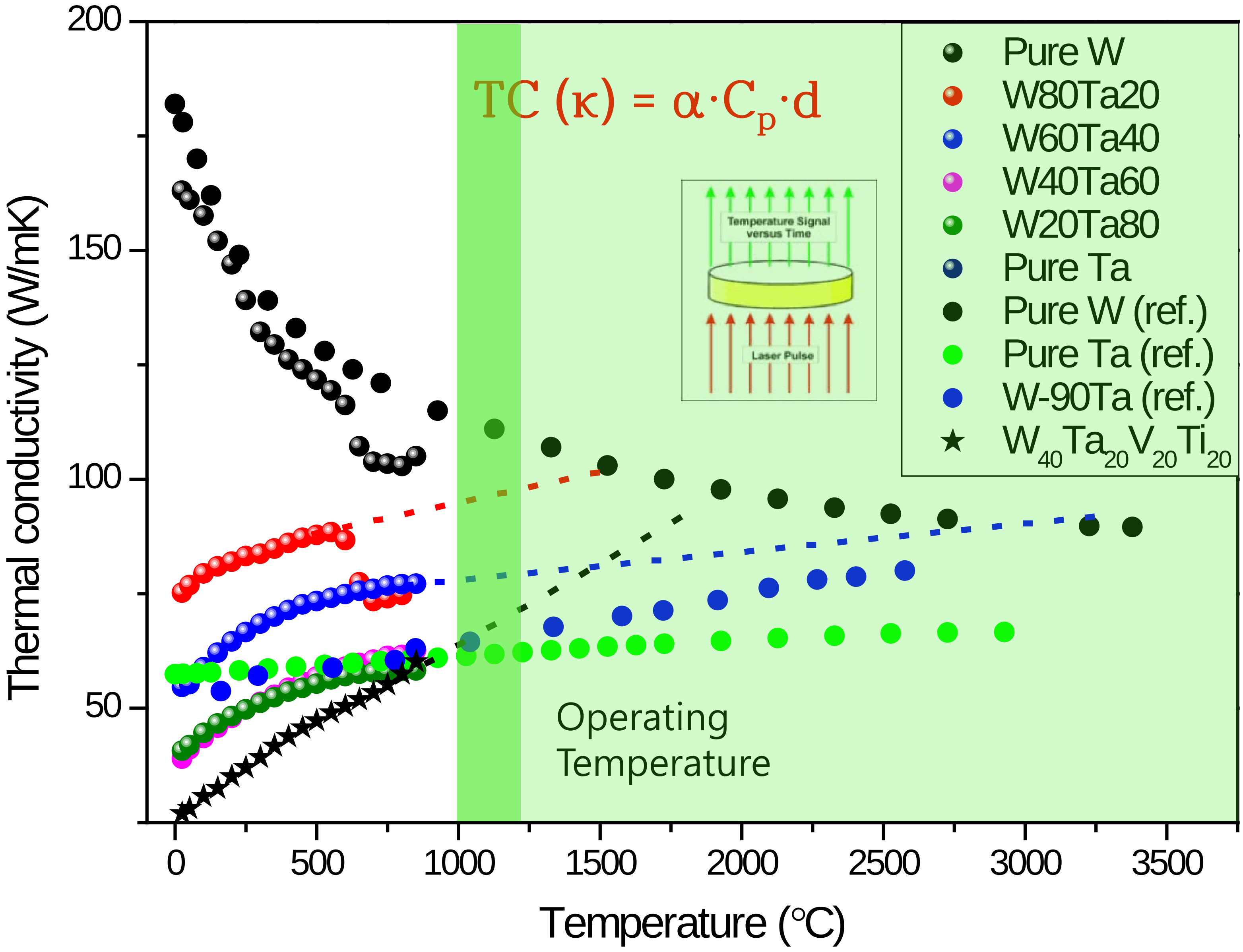
Thermal Conductivity





- Thermal conductivity is important factor for durability
- Alloying can deteriorate thermal conductivity severely
- High entropy alloy concept will recover these thermal conductivity

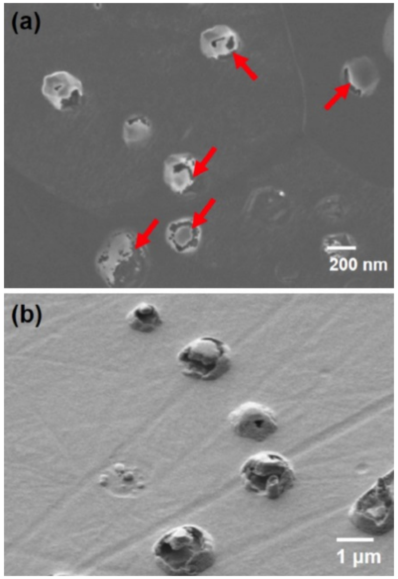
Results of Thermal Conductivity



3. Irradiation properties: Outline

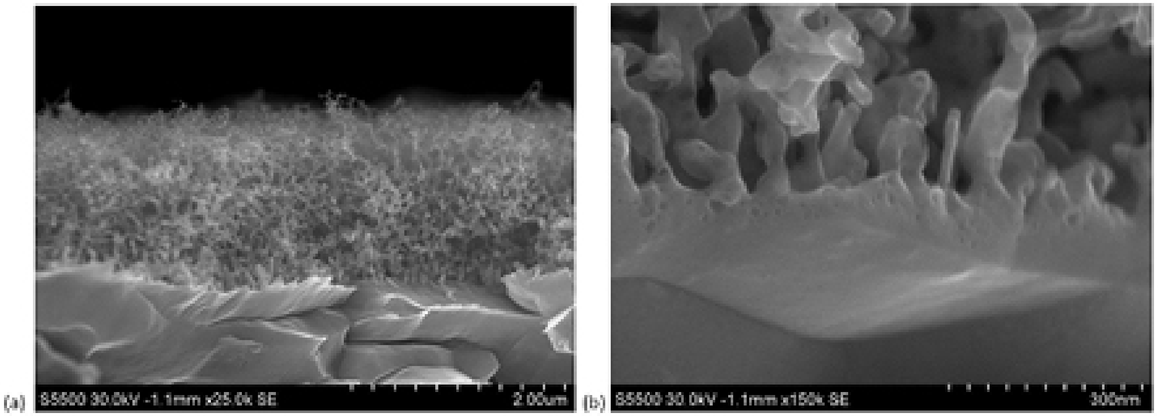
Ion beam effect on tungsten

D ion irradiation



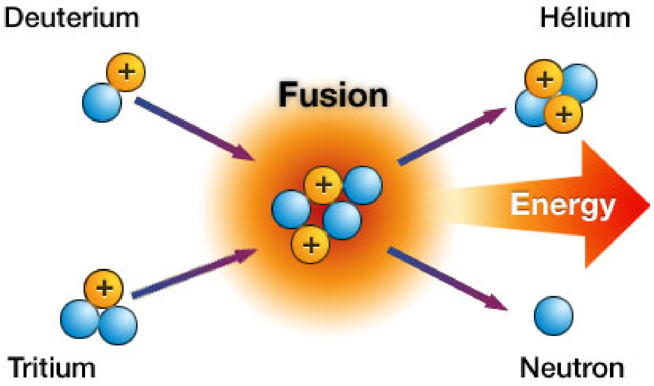
Jaemin Song, et al., Fusion Engineering and Design, 2016

He ion irradiation



fuzz-like nanostructures

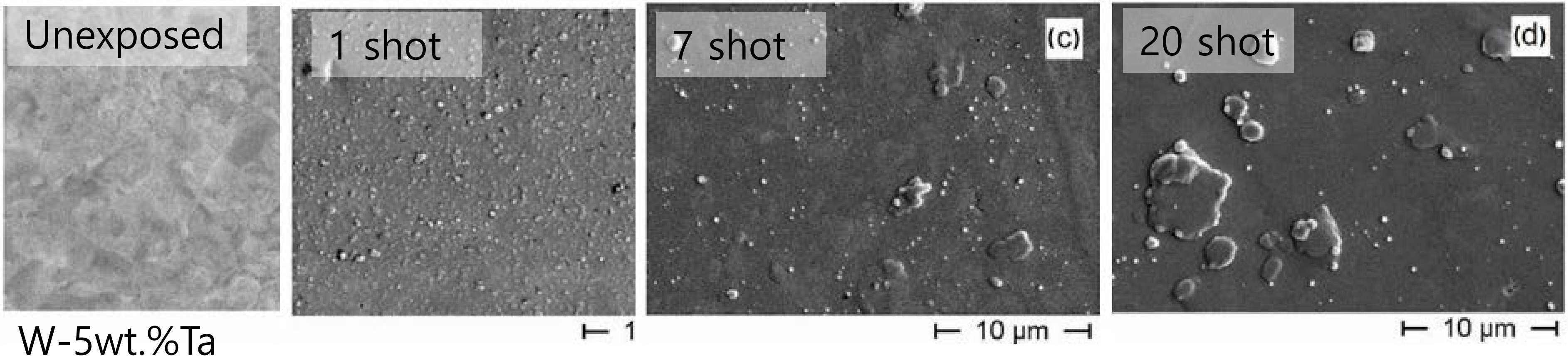
Yu. Gasparyan, Nuclear Fusion, 2016



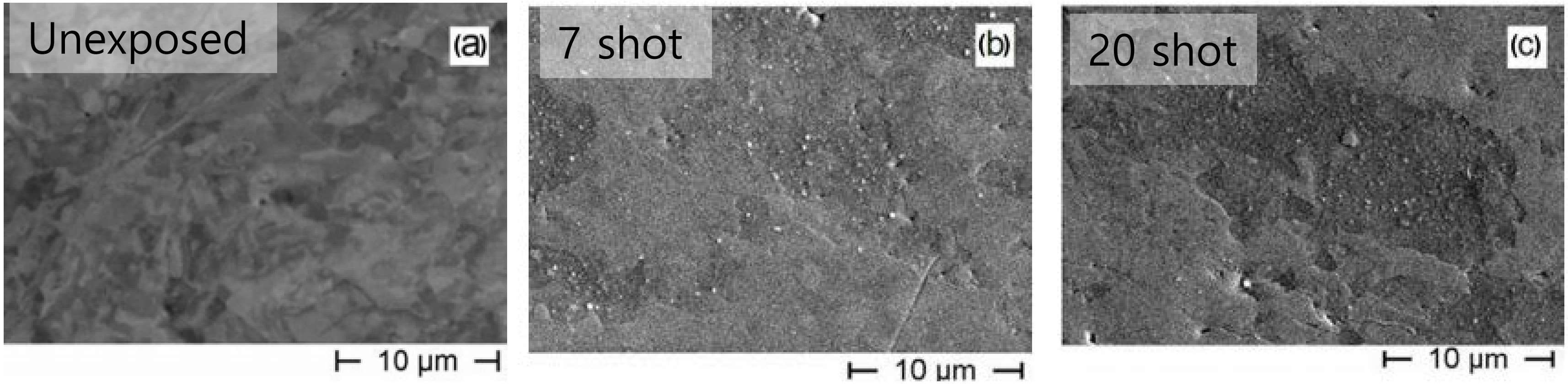
- Microstructure change by plasma irradiation must be investigated

Ion beam effect on tungsten alloys

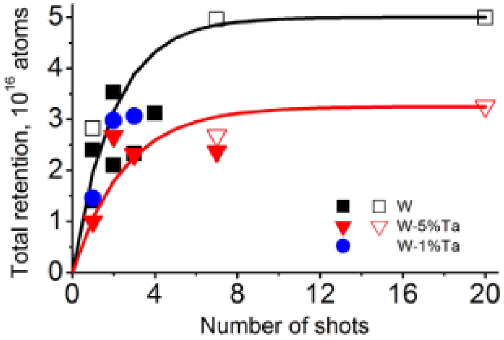
Pure W



W-5wt.%Ta



D_2 retention measurement (TDS; Thermal Desorption Spectroscopy)
: Measuring interstitial D_2

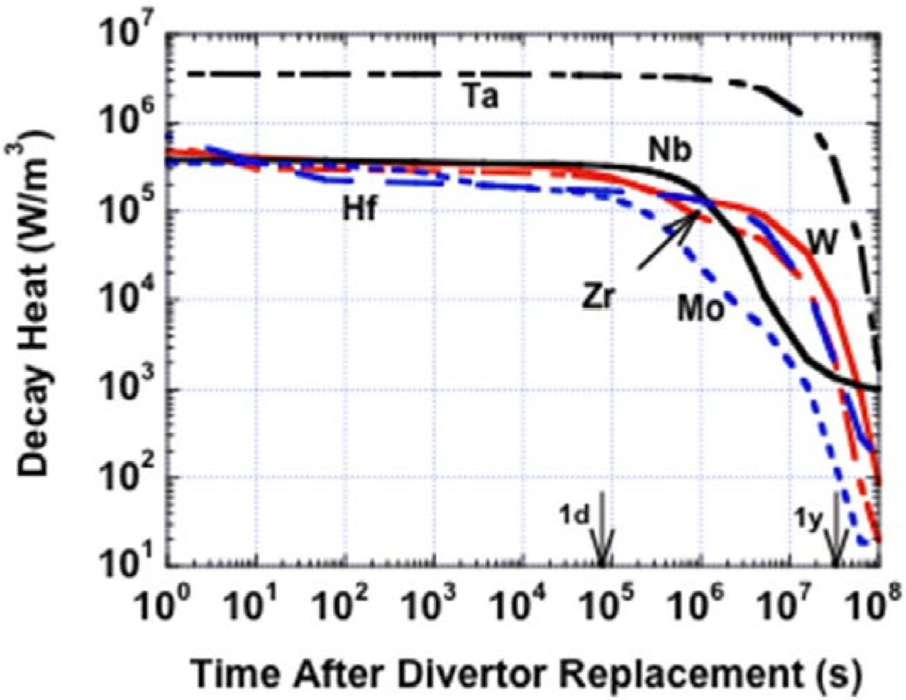


D_2 retention ↑
Blistering ↑

Conclusion

- 핵융합로는 미래 에너지원으로 각광을 받고 있고 현재 사용화를 위한 여러 연구가 진행 중에 있다.
- 텅스텐 합금의 핵융합로 플라즈마 대면소재로의 사용 가능성을 알아보았다.
- 순텅스텐의 기계적 성질 향상을 위한 intrinsic property의 조절로 활용 가능한 원소들을 선정하였으며, 저방사화 원소인 Ta, V, Ti, Cr 원소를 선정하였다.
- 하이엔트로피 합금 컨셉을 이용하여 아크 멜팅을 통하여 합금화하였으며, 이에 따른 물성 측정을 실행하였다.
- 고온 물성의 경우 순텅스텐 보다 큰 강화효과를 관찰하였으며, 이는 고용강화효과에 영향을 받으며, Dynamic strain aging 효과도 있는 것으로 보고 연구를 진행 중에 있다.
- 고온 열물성 측정을 위한 Electrostatic Levitation 측정을 진행하였으며, 고온 영역에서 과냉각 영역을 측정하는데 성공하였다.
- 고온 열전도도 실험을 통하여 순텅스텐은 고온에서 열전도도가 감소하는데 반하여, 합금화 정도가 커질 수록 열전도도가 증가함을 이용하여 Operating Temperature에서의 열물성을 조절 가능할 것으로 보인다.
- 이온 조사 실험을 통하여 조사 성질이 크게 변하지 않는 합금제작에 가능성이 있을 것으로 판단된다.

Decay heat



Refractory elements have higher decay heat than Low-Z elements
Ta has 1000 times higher decay heat than other elements
: active cooling needed