SEOUL NATIONAL UNIVERSITY

High entropy alloy

Current Status of Structural Materials

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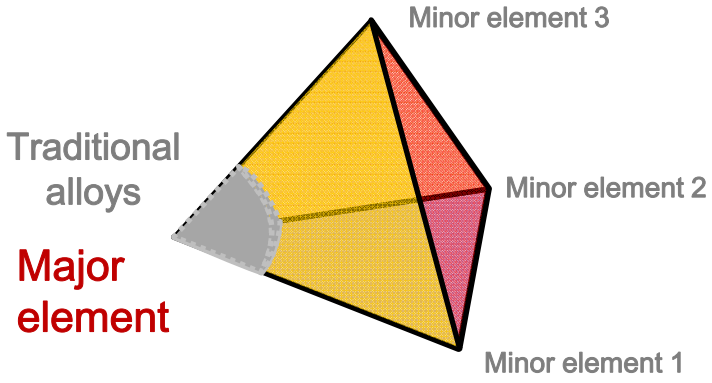
High entropy alloy : definition

High entropy alloy containing at least five principal elements, each having the atomic percentage between 5 % and 35 %.

$$\Delta S_{conf} = -klnw = -R\left(\frac{1}{n}ln\frac{1}{n} + \frac{1}{n}ln\frac{1}{n} + \cdots + \frac{1}{n}ln\frac{1}{n}\right) = -Rln\frac{1}{n} = Rln(n)$$

Table I. Configurational entropies of equimolar alloys with constituent elements up to 13

n	1	2	3	4	5	6	7	8	9	10	11	12	13
ΔS_{conf}	0	0.69R	1.1R	1.39R	1.61R	1.79R	1.95R	2.08R	2.2R	2.3R	2.4R	2.49R	2.57R



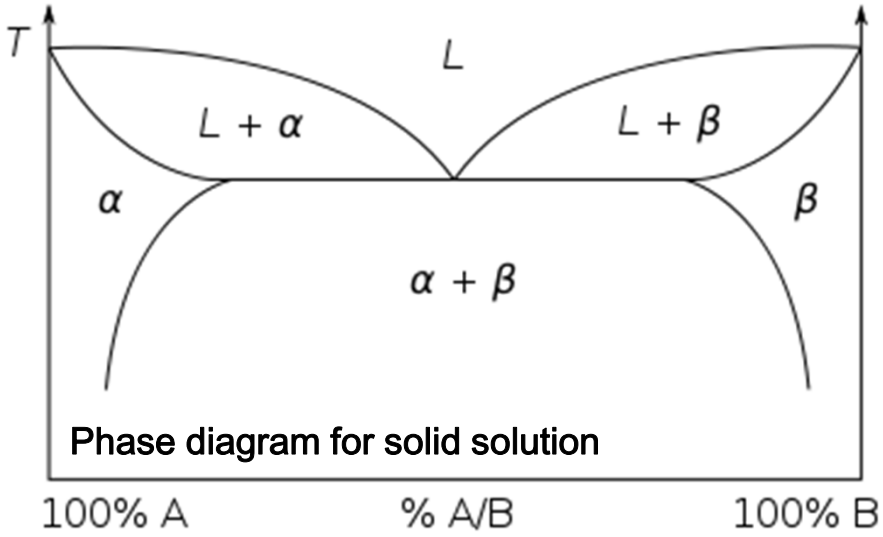
Conventional alloy system

Ex) 304 steel - $Fe_{74}Cr_{18}Ni_8$

Table II. Configurational entropies calculated for typical traditional alloys at their liquid state or random state

Systems	Alloys	ΔS_{conf} at liquid state
Low-alloy steel	4340	0.22R low
Stainless steel	304	0.96R low
	316	1.15R medium
High-speed steel	M2	0.73R low
Mg alloy	AZ91D	0.35R low
Al alloy	2024	0.29R low
	7075	0.43R low
Cu alloy	7-3 brass	0.61R low
Ni-base superalloy	Inconel 718	1.31R medium
	Hastelloy X	1.37R medium
Co-base superalloy	Stellite 6	1.13R medium
BMG	$Cu_{47}Zr_{11}Ti_{34}Ni_8$	1.17R medium
	$Zr_{53}Ti_5Cu_{16}Ni_{10}Al_{16}$	1.30R medium

Unique properties of high entropy alloy

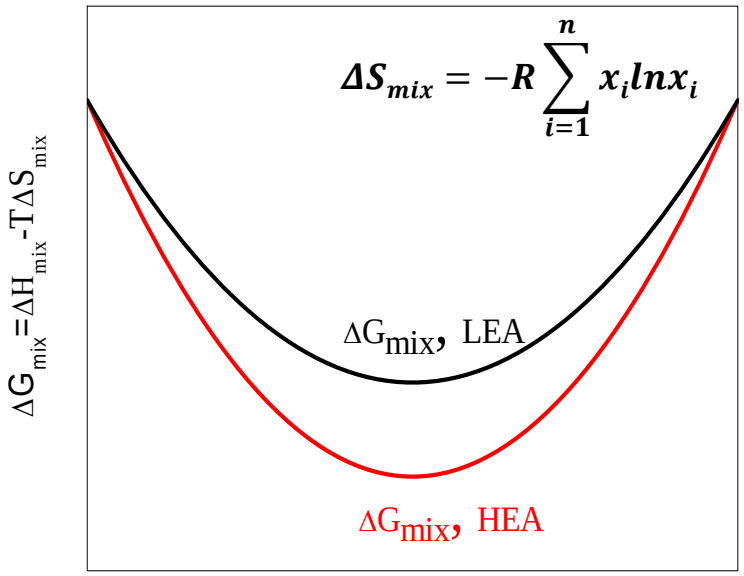


Solid solution

: relatively stabilized by significantly high entropy of mixing, especially at high temperature

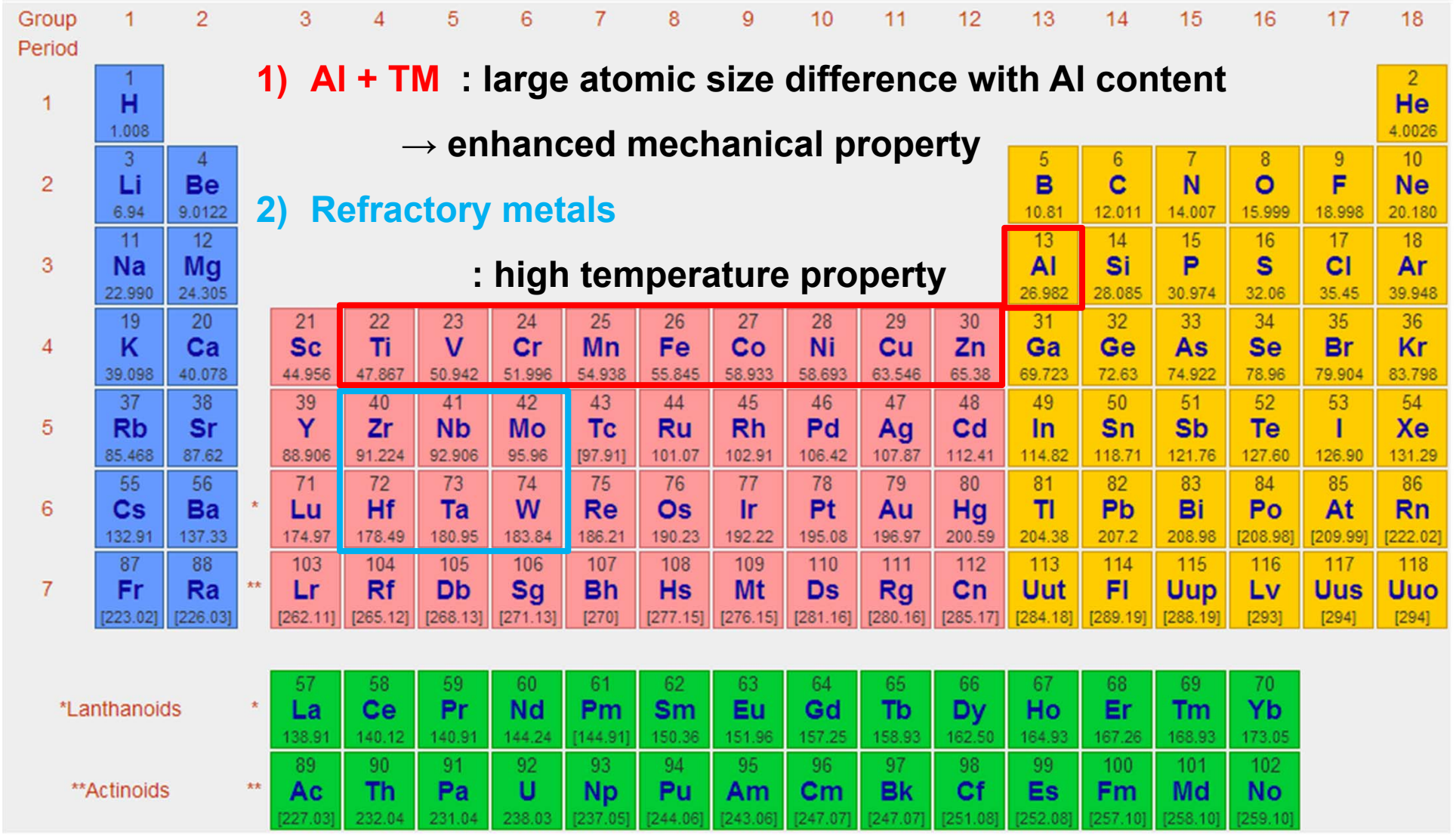
Excellent high temperature property

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



Especially at high temperature, HEA is more stable than LEA

Previous works for high entropy alloy system



Core effect for high entropy alloy

(1) Thermodynamic : high entropy effect

(2) Kinetics : sluggish diffusion effect

(3) Structure : severe lattice distortion effect

(4) Property : cocktail effect

Core effect for high entropy alloy

(1) Thermodynamic : high entropy effect

: interfere with complex phase formation

Competing state :

1) Elemental phase : terminal solid solution based on one metal element

2) Intermetallic compound : stoichiometric compounds having specific superlattices

3) Solid solution : the phase with the complete mixing of all elements or with a significant mixing of constituent elements in the structure of BCC, FCC, and HCP

Table III. Comparisons of ΔH_{mix}, ΔS_{mix}, and ΔG_{mix} between elemental phases, compounds, and solid solutions

Possible states	Elemental phases	Compounds	Solid solutions
ΔH_{mix}	~ 0	Large negative	Medium negative
$-T\Delta S_{mix}$	~ 0	~ 0	$-RT\ln(n)$
ΔG_{mix}	~ 0	Large negative	Large negative

Strain energy from atomic size difference is not included in ΔH_{mix}.

Core effect for high entropy alloy

(1) Thermodynamic : high entropy effect

: interfere with complex phase formation

Exceptional case for Gibbs phase rule (F=C-P+1)

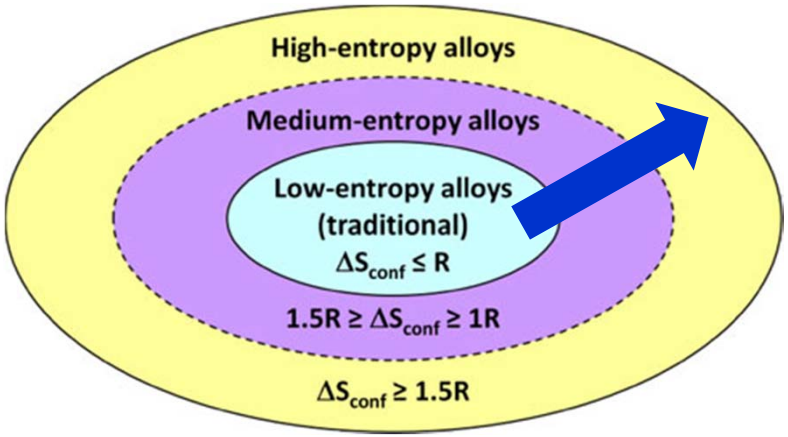
- conventional alloy : maximum number of phase possible to form

$P = C+1$

- high entropy alloy : single phase solid solution is dominant

total number of phase to form $\ll P_{max}$

(Gibbs phase rule)



A higher number of elements

➡ Random state

1) to have the mixing enthalpy closer to that of the completely ordered state

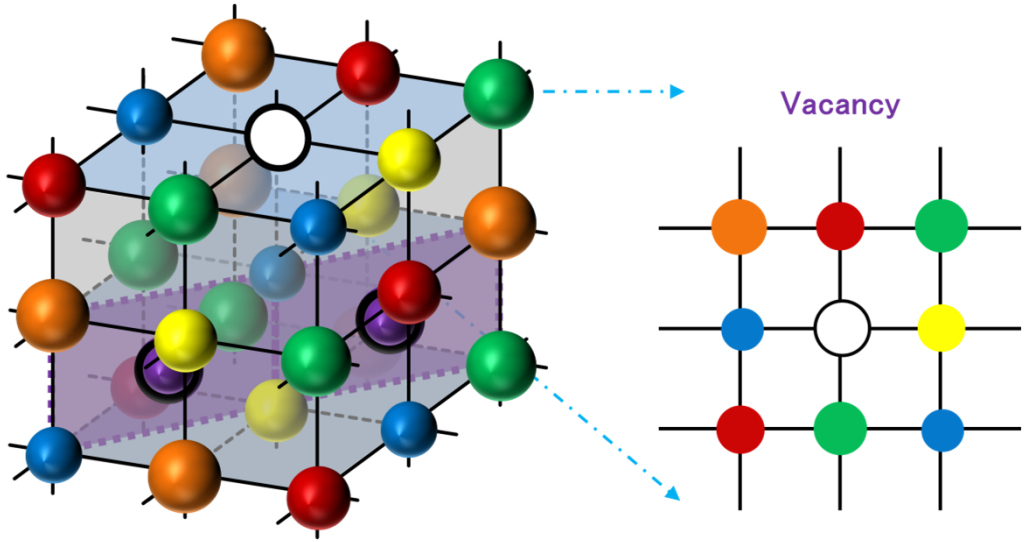
2) to become even more competitive with the ordered state under the aid of its high mixing entropy

Core effect for high entropy alloy

(2) Kinetics : sluggish diffusion effect

: slow down phase transformation

Formation of new phases requires cooperative diffusion of many different kinds of atoms to accomplish the partitioning of composition in HEAs



A vacancy in the whole-solute matrix is surrounded and competed by different element atoms during diffusion

→ slow diffusion & higher activation energy

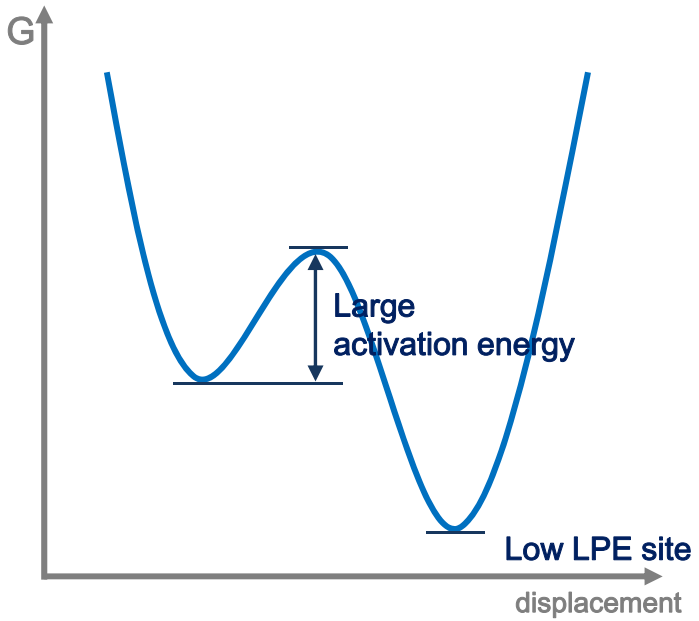
(larger fluctuation of lattice potential energy between lattice sites)

Core effect for high entropy alloy

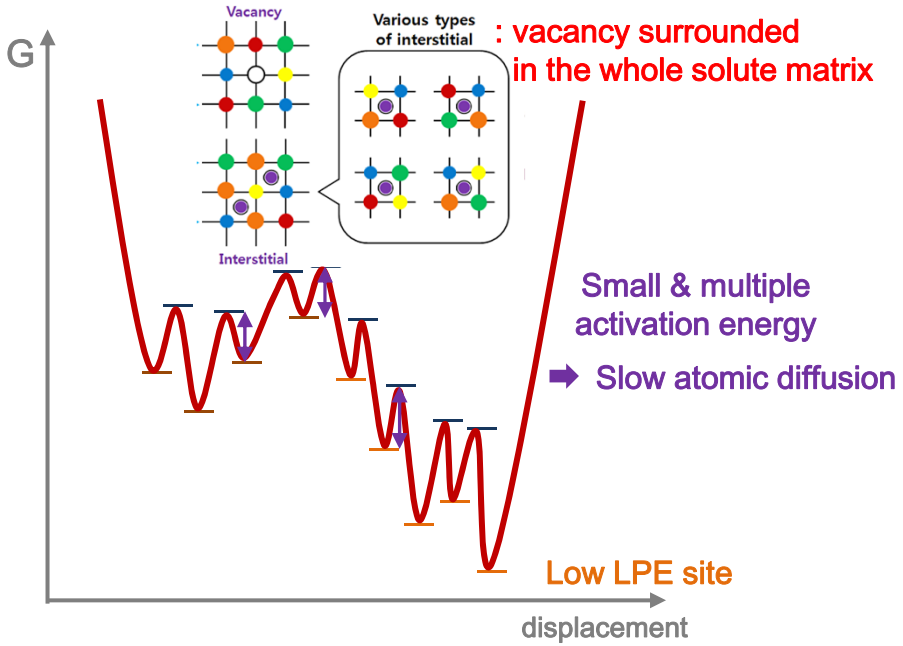
(2) Kinetics : sluggish diffusion effect

: slow down phase transformation

Single-component system



Multi-component equiatomic system



The abundant low lattice potential energy (LPE) sites can serve as traps and hinder atomic diffusion, leading to the sluggish diffusion effect

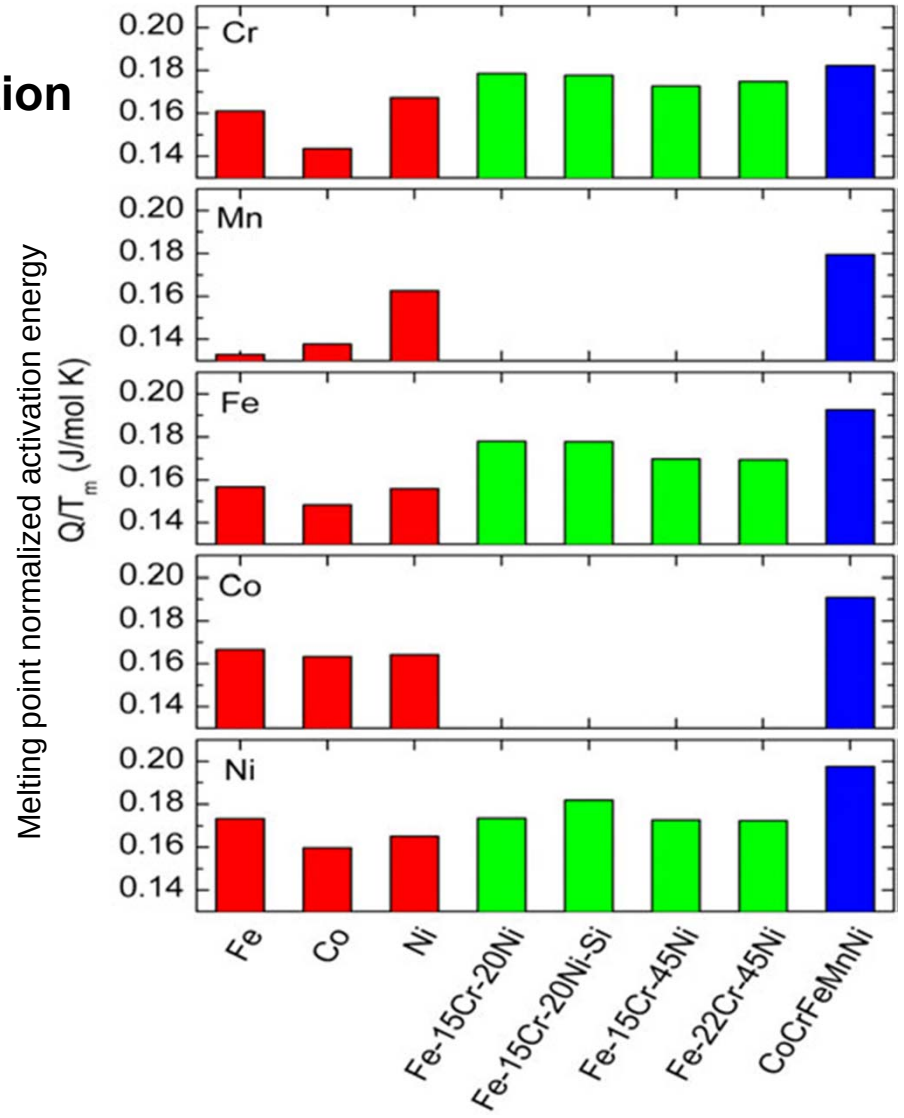
Core effect for high entropy alloy

(2) Kinetics : sluggish diffusion effect

: slow down phase transformation

Experiment to verify this : a near ideal solution system of Co-Cr-Fe-Mn-Ni with stable single fcc solid solution to make diffusion couples

(Q/T_m)HEA ≫ (Q/T_m)Fe-Cr-Ni(-Si) > (Q/T_m)pure metal



Core effect for high entropy alloy

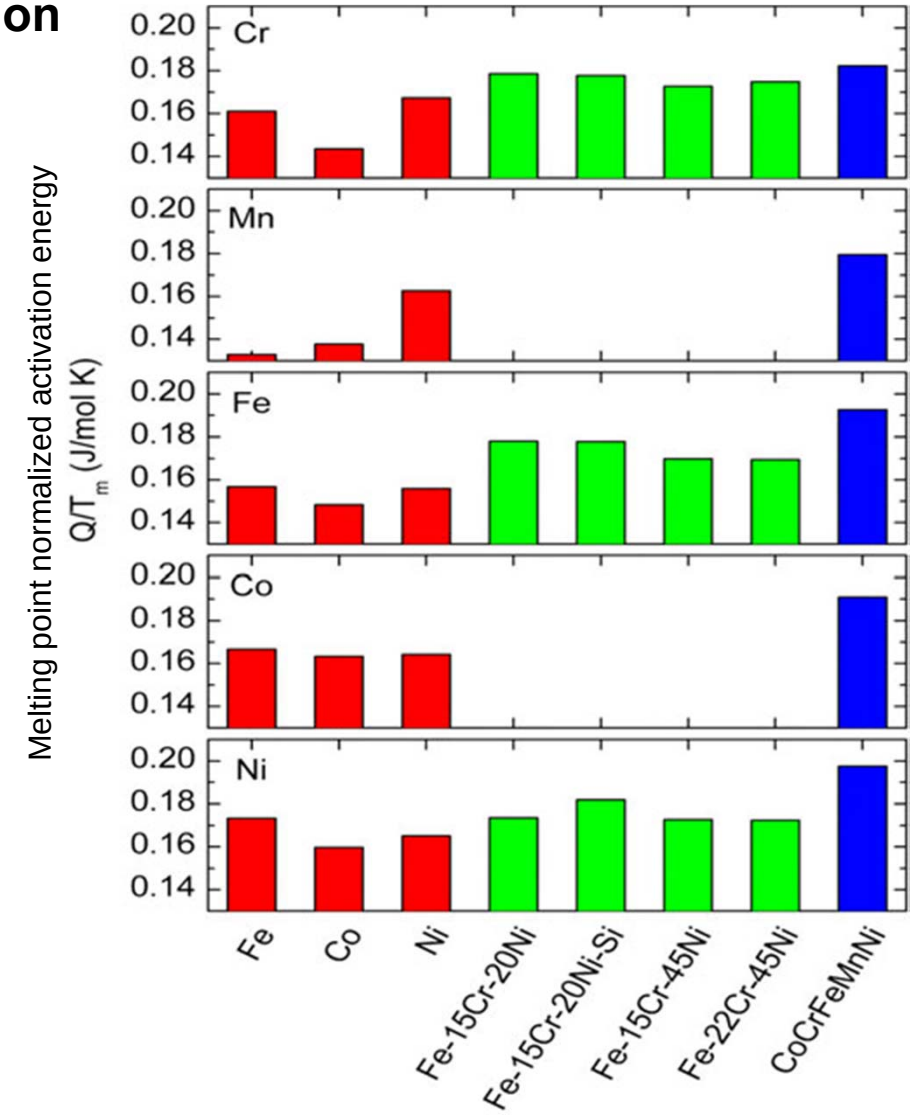
(2) Kinetics : sluggish diffusion effect

: slow down phase transformation

Easy to get

1) **Supersaturated state**
2) **Fine precipitates,**
3) **Increased recrystallization temperature**
4) **Slower grain growth**
5) **Reduced particle coarsening rate**
6) **Increased creep resistance**

Microstructure and property control for better performance



Core effect for high entropy alloy

(3) Structure : severe lattice distortion effect

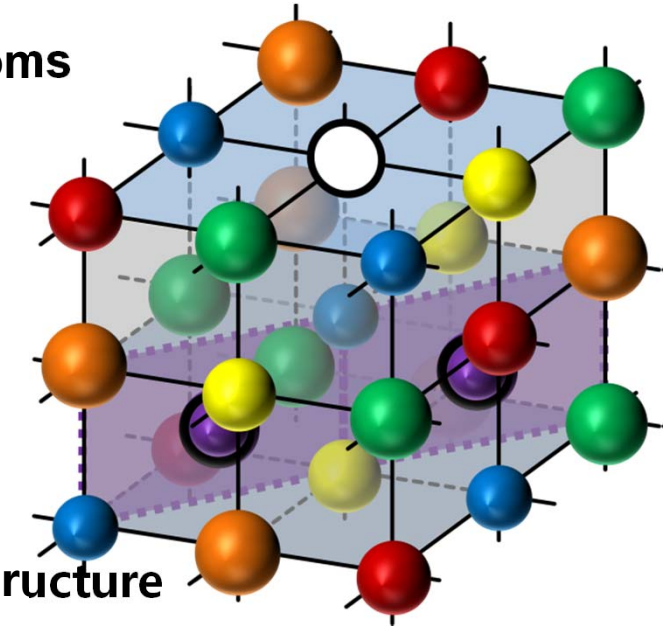
: alter properties to an extent

Multi-element matrix of each solid solution phase in HEAs

: whole-solute matrix

Every atom is surrounded by different kinds of atoms and thus suffers lattice strain and stress

1) **Atomic size difference**
2) **Different bonding energy**
3) **Different crystal structure**



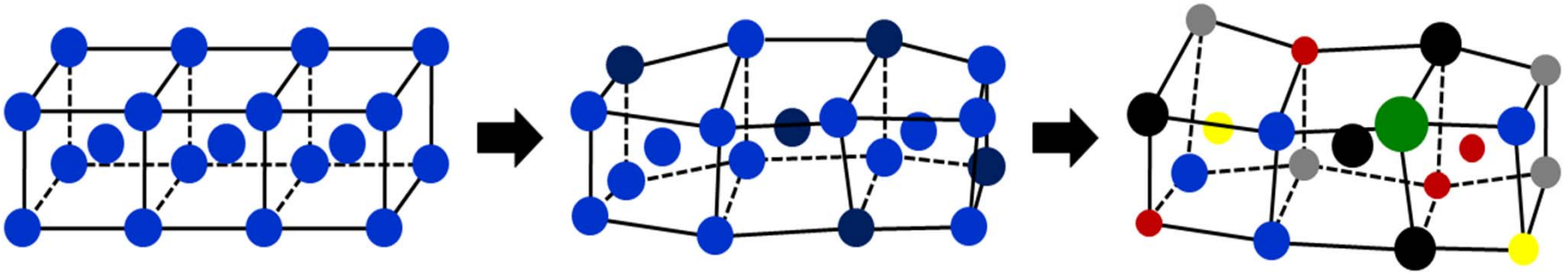
- **non-symmetrical bindings & electronic structure**
- **higher lattice distortion**

Yong Zhang et al., Adv. Eng. Mat. P534-538, 2008

Core effect for high entropy alloy

(3) Structure : severe lattice distortion effect

: alter properties to an extent



Yong Zhang et al., Adv. Eng. Mat. P534-538, 2008

Lattice distortion

1) Affects properties

- **Large solution hardening in the heavily distorted lattice**

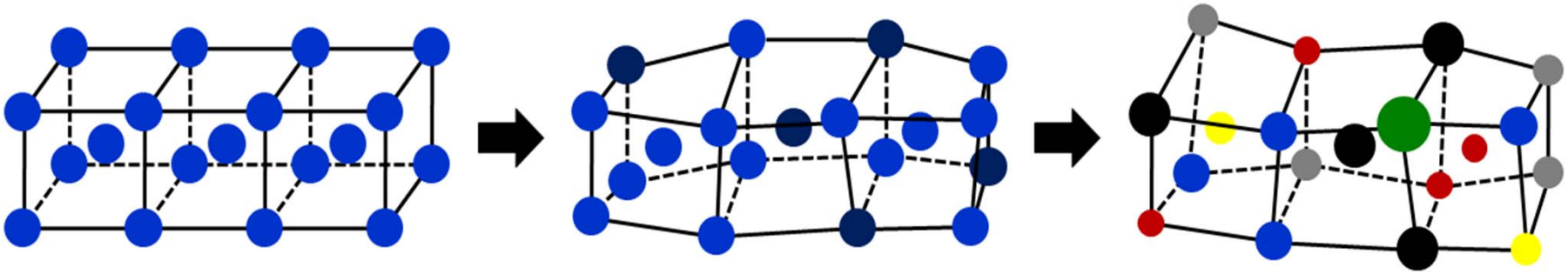
  ➡ **Hardness and strength effectively increase**

Vickers hardenss	Mixture rule [MPa]	HEA [MPa]
NbMoTaW	1,790	4,455
VNbMoTaW	1,557	5,250

Core effect for high entropy alloy

(3) Structure : severe lattice distortion effect

: alter properties to an extent



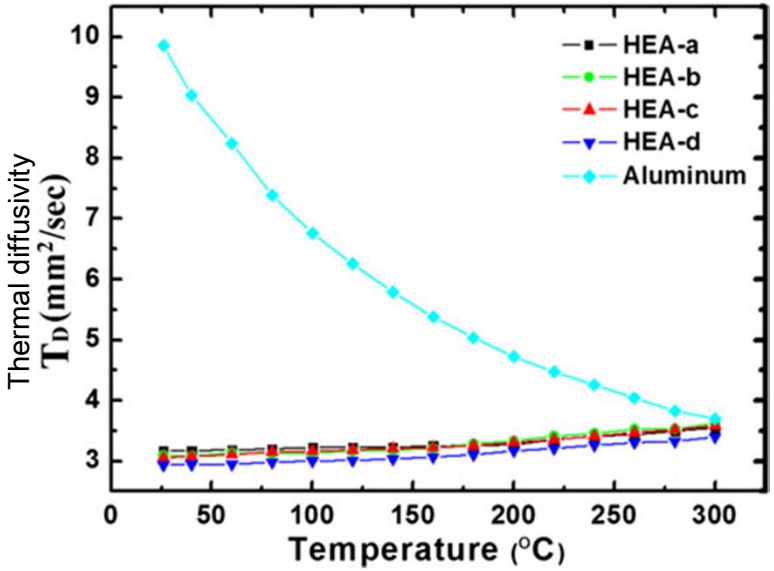
Yong Zhang et al., Adv. Eng. Mat. P534-538, 2008

Lattice distortion

2) Reduces the thermal effect on properties

: electrical and thermal conductivity significantly decrease (∵ electron and phonon scattering)

Lattice distortion caused by thermal vibration of atoms is relatively small

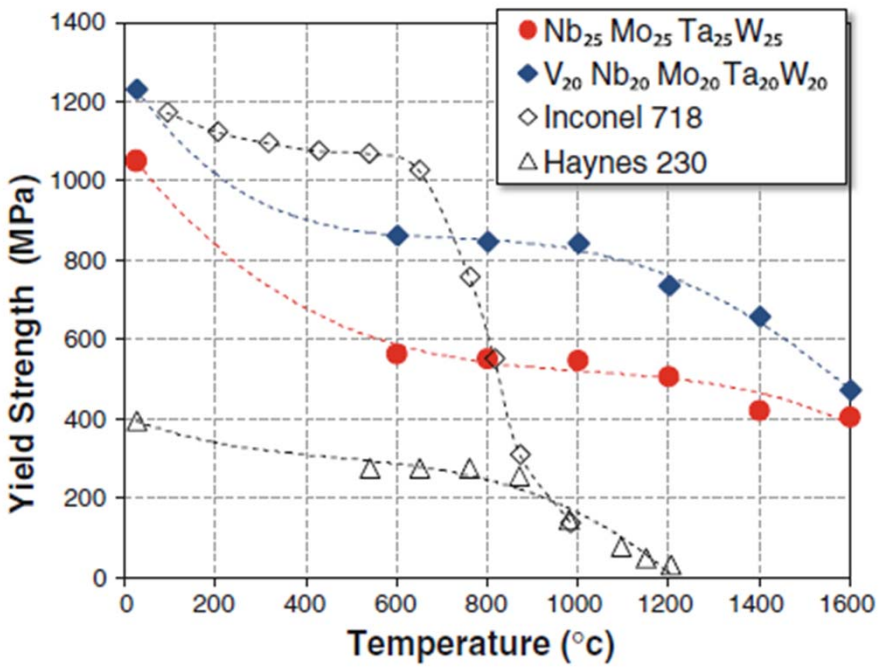


a = $Al_{0.3}CrFe_{1.5}MnNi_{0.5}$, b = $Al_{0.5}CrFe_{1.5}MnNi_{0.5}$
c = $Al_{0.3}CrFe_{1.5}MnNi_{0.5}Mo_{0.1}$, d = $Al_{0.5}CrFe_{1.5}MnNi_{0.5}Mo_{0.1}$

Core effect for high entropy alloy

(4) Property : cocktail effect

: bring excess quantities to the quantities predicted by the mixture rule due to mutual interactions of unlike atoms and severe lattice distortion



At least five major elements are used to enhance the properties of the materials

$Property_{total}$ = Property A + Property B + Property C +⋯

By the effect of phase shape, phase distribution, phase boundaries, and properties of each phase

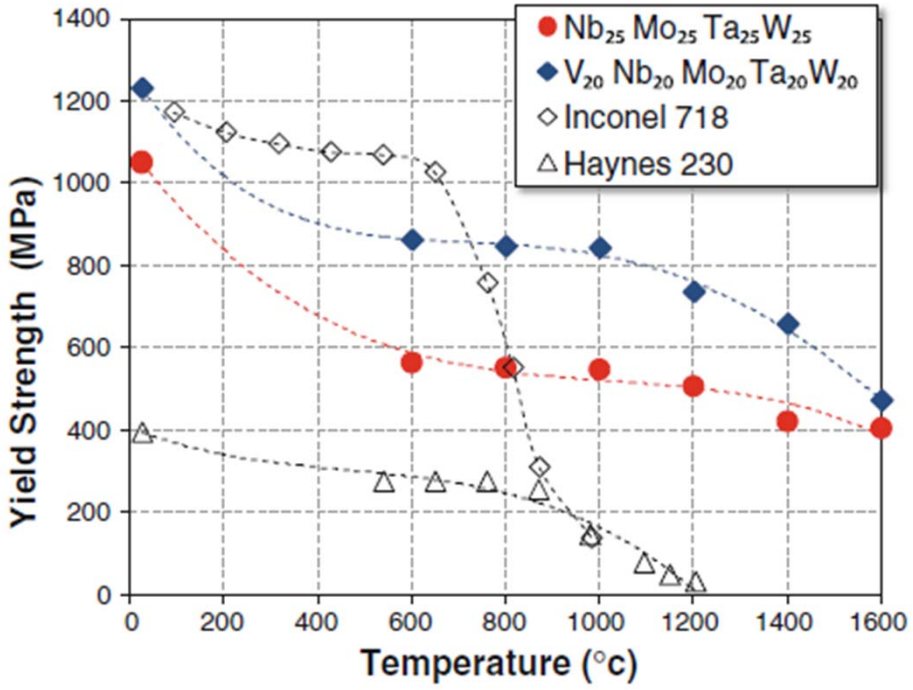
each phase : a multi-element solid solution

→ atomic scale composites!!

Core effect for high entropy alloy

(4) Property : cocktail effect

: bring excess quantities to the quantities predicted by the mixture rule due to mutual interactions of unlike atoms and severe lattice distortion



1) Mechanical property is sustained at even high temperature
2) Refractory HEA has an excellent mechanical property compared with Haynes 230

Refractory high entropy alloy

➧ potential applications at very high temperature

Inconel 718 : $Ni_{50}Cr_{17}Mo_{2.8}Nb_{4.75}$

Haynes 230 : $Ni_{57}Cr_{22}W_{14}Co_5Mo_2$

Thanks for your kind attention.