

High entropy alloy

Current Status of Structural Materials

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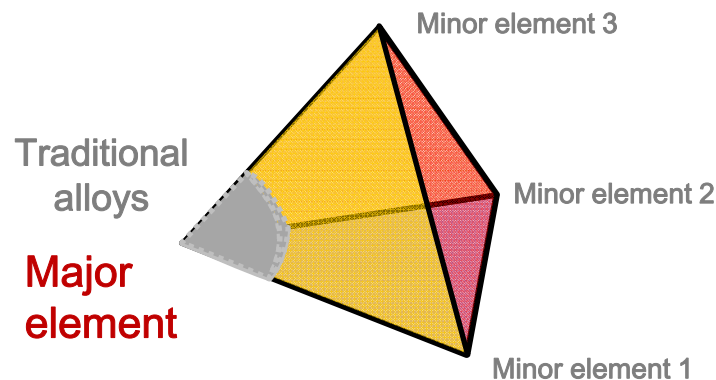
High entropy alloy : definition

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

$$\Delta S_{conf} = -k \ln w = -R \left(\frac{1}{n} \ln \frac{1}{n} + \frac{1}{n} \ln \frac{1}{n} + \dots + \frac{1}{n} \ln \frac{1}{n} \right) = -R \ln \frac{1}{n} = R \ln(n)$$

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	$0.69R$	$1.1R$	$1.39R$	$1.61R$	$1.79R$	$1.95R$	$2.08R$	$2.2R$	$2.3R$	$2.4R$	$2.49R$	$2.57R$



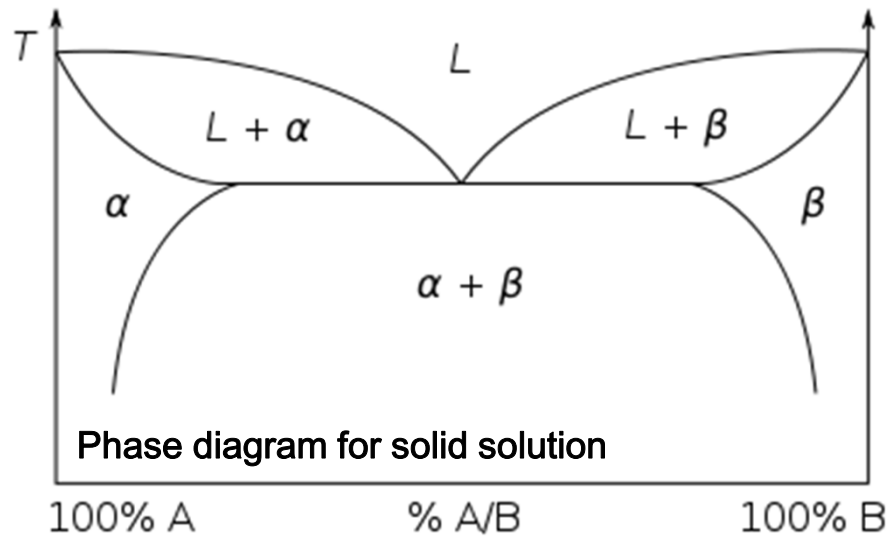
Conventional alloy system

Ex) 304 steel - $\text{Fe}_{74}\text{Cr}_{18}\text{Ni}_8$

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	$\text{Cu}_{47}\text{Zr}_{11}\text{Ti}_{34}\text{Ni}_8$	$1.17R$ medium
	$\text{Zr}_{53}\text{Ti}_5\text{Cu}_{16}\text{Ni}_{10}\text{Al}_{16}$	$1.30R$ medium

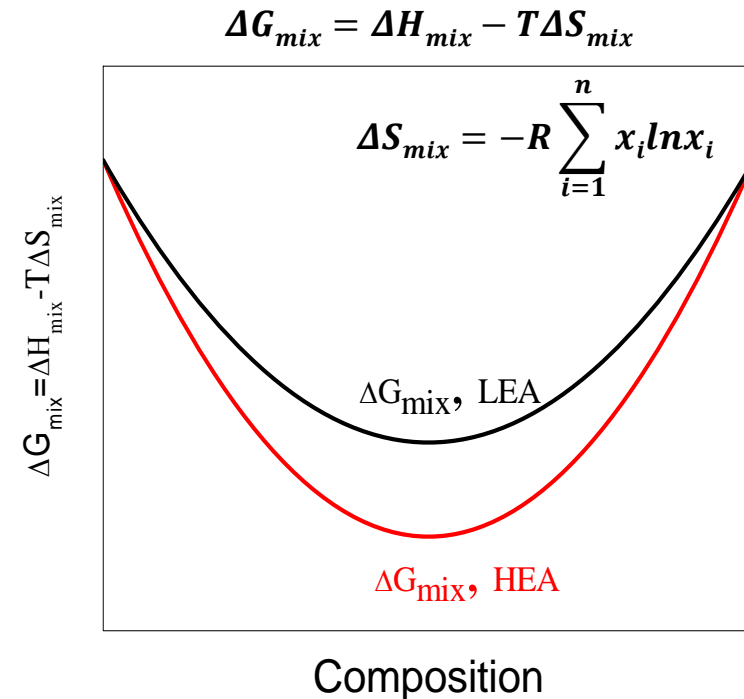
Unique properties of high entropy alloy



Solid solution

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

➡ Excellent high temperature property



➡ Especially at high temperature, HEA is more stable than LEA

Previous works for high entropy alloy system

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																		
1	1 H 1.008																	2 He 4.0026
2	3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
3	11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
4	19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	* 71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
7	87 Fr [223.02]	88 Ra [226.03]	** 103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Uut [284.18]	114 Fl [289.19]	115 Uup [288.19]	116 Lv [293]	117 Uus [294]	118 Uuo [294]
*Lanthanoids			* 57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05		
**Actinoids			** 89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]		

1) **Al + TM** : large atomic size difference with Al content

→ enhanced mechanical property

2) **Refractory metals**

: high temperature property

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
$-T\Delta S_{\text{mix}}$	~ 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 $\ll P_{\max}$

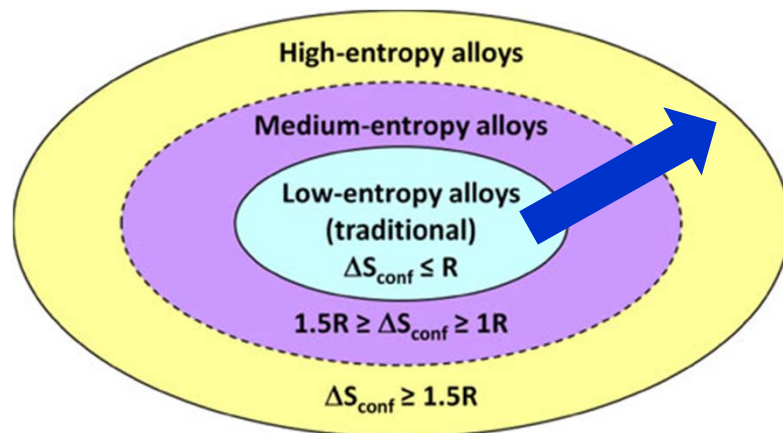
(Gibbs phase rule)

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

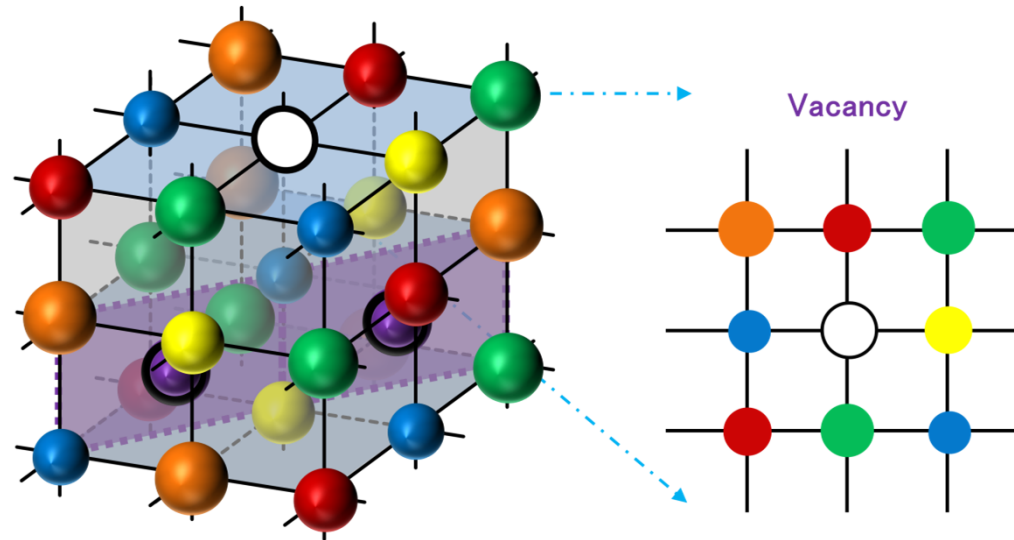


Core effect for high entropy alloy

(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

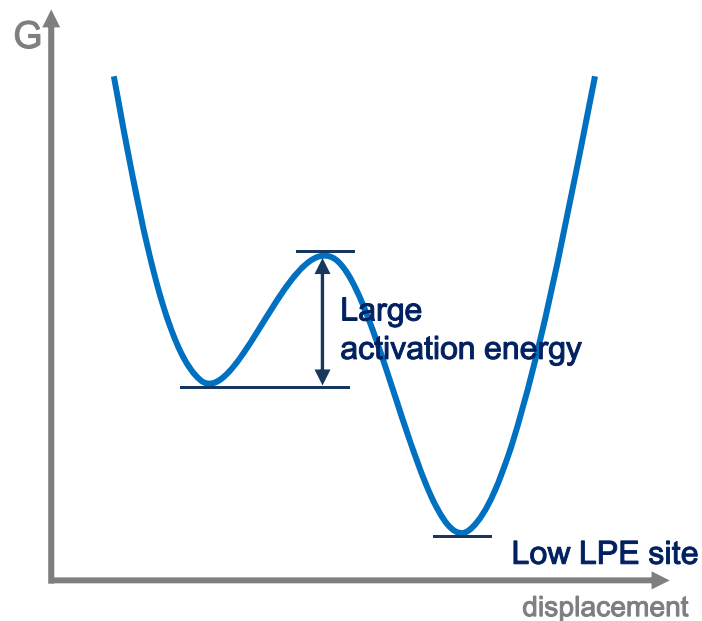
→ slow diffusion & higher activation energy

(larger fluctuation of lattice potential energy between lattice sites)

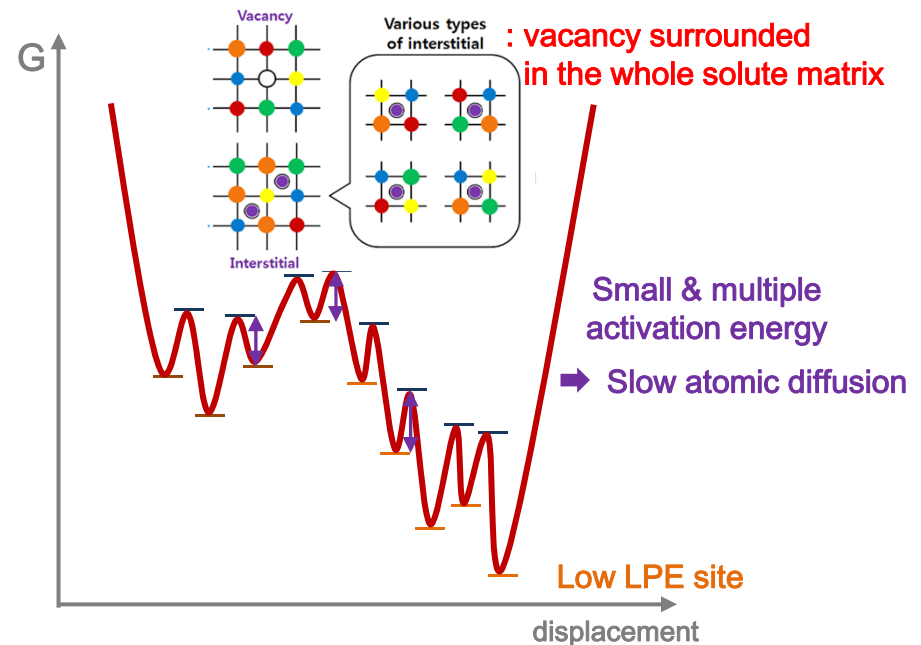
Core effect for high entropy alloy

(2) Kinetics : sluggish diffusion effect : slow down phase transformation

Single-component system



Multi-component equiatomic system



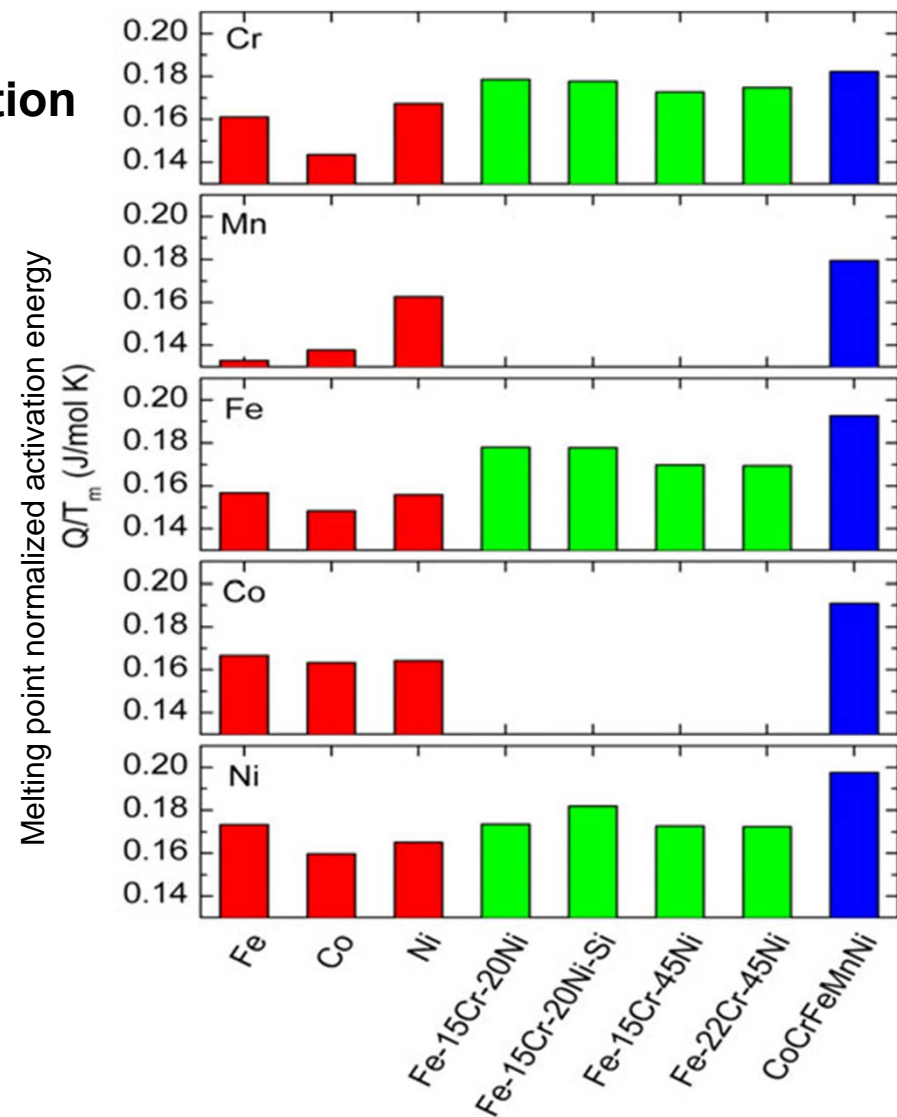
The abundant low lattice potential energy (LPE) sites can serve as traps and hinder atomic diffusion, leading to the sluggish diffusion effect

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

$(Q/T_m)_{\text{HEA}} \gg (Q/T_m)_{\text{Fe-Cr-Ni(-Si)}} >$
 $(Q/T_m)_{\text{pure metal}}$



Core effect for high entropy alloy

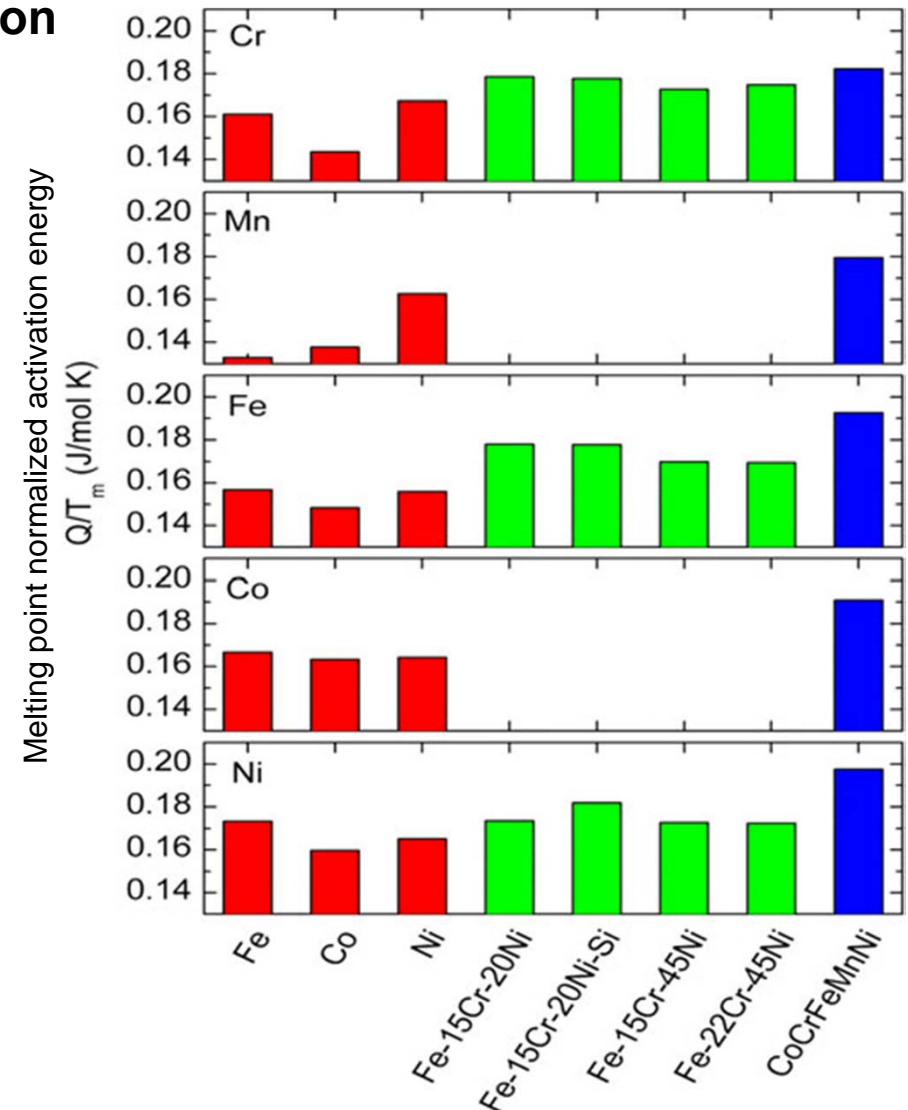
(2) Kinetics : sluggish diffusion effect
: slow down phase transformation

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

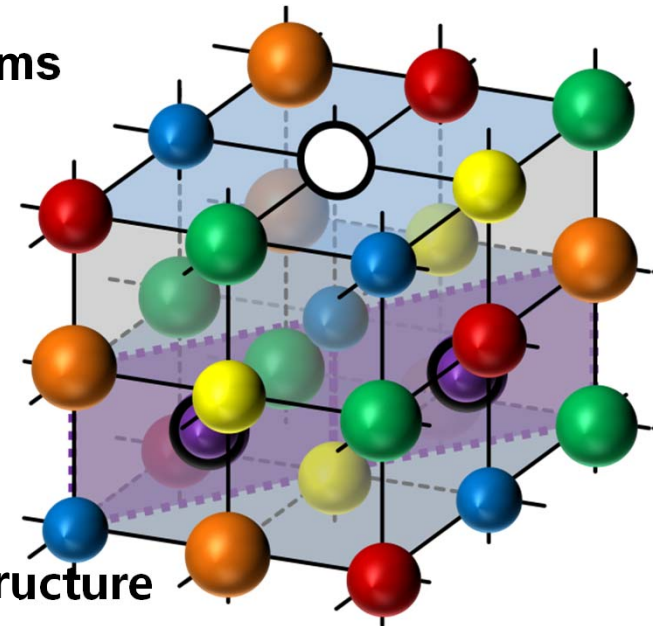
(3) Structure : severe lattice distortion effect
: alter properties to an extent

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**

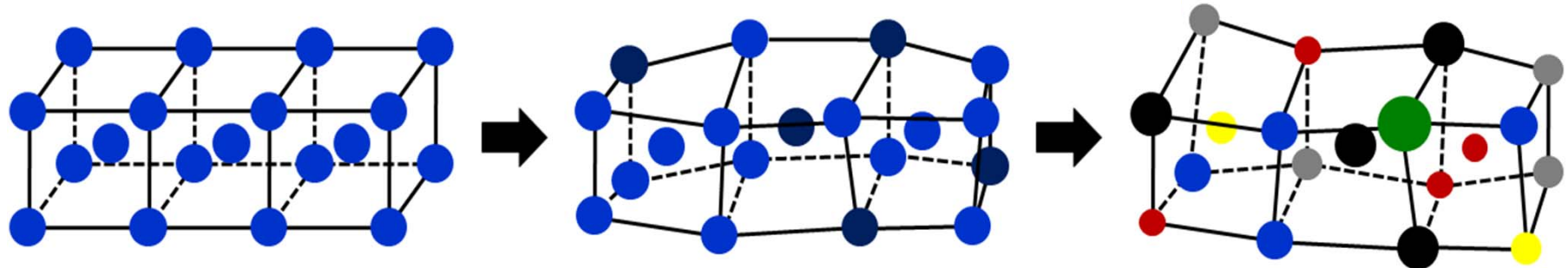
- 1) Atomic size difference**
- 2) Different bonding energy**
- 3) Different crystal structure**

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



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

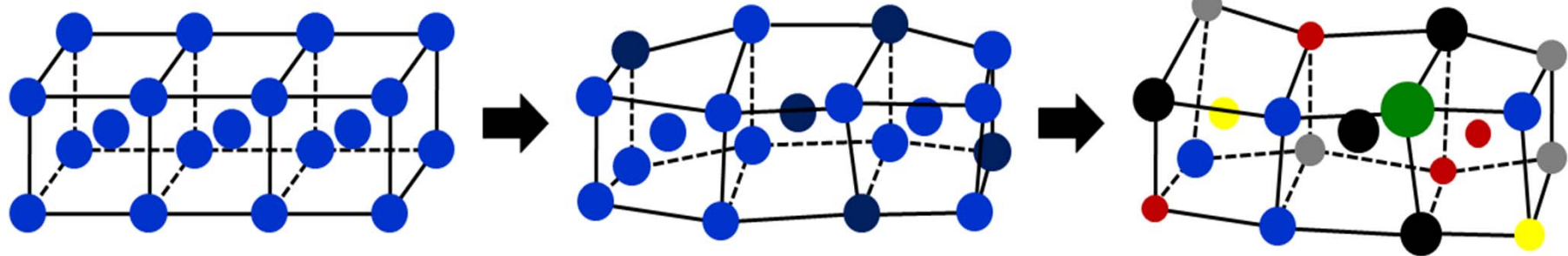
1) Affects properties

- 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

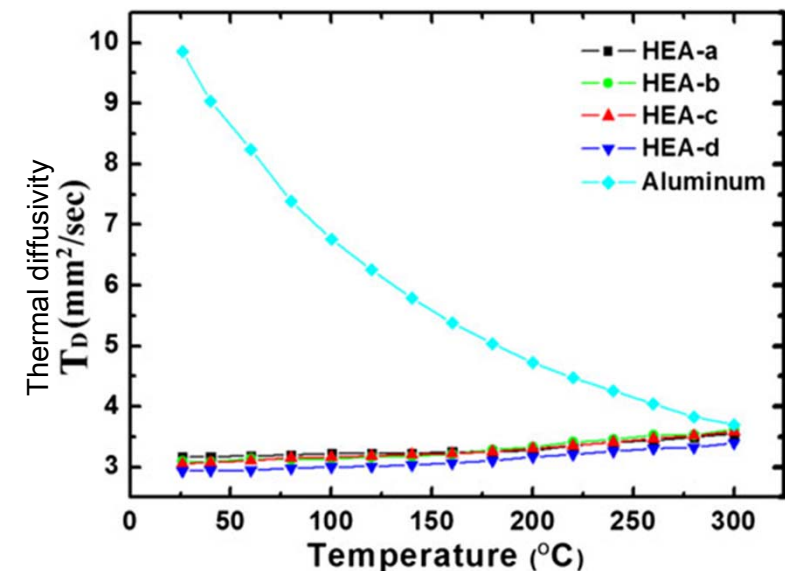


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Lattice distortion

2) Reduces the thermal effect on properties
: electrical and thermal conductivity
significantly decrease (\because electron and
phonon scattering)

**Lattice distortion caused by thermal
vibration of atoms is relatively small**

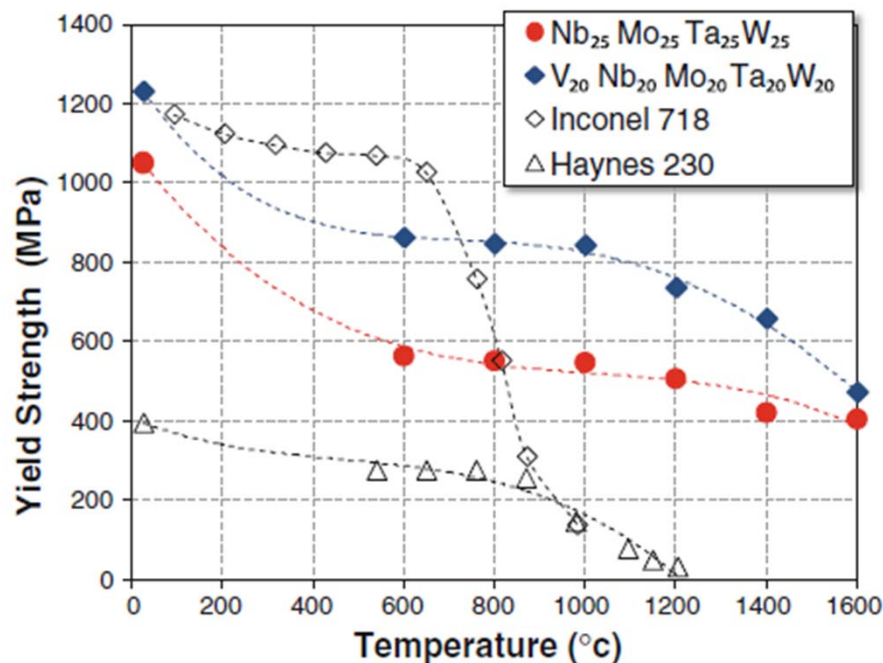


a = $\text{Al}_{0.3}\text{CrFe}_{1.5}\text{MnNi}_{0.5}$, b = $\text{Al}_{0.5}\text{CrFe}_{1.5}\text{MnNi}_{0.5}$
c = $\text{Al}_{0.3}\text{CrFe}_{1.5}\text{MnNi}_{0.5}\text{Mo}_{0.1}$, d = $\text{Al}_{0.5}\text{CrFe}_{1.5}\text{MnNi}_{0.5}\text{Mo}_{0.1}$

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

$\text{Property}_{\text{total}} = \text{Property A} + \text{Property B} + \text{Property C} + \dots$

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

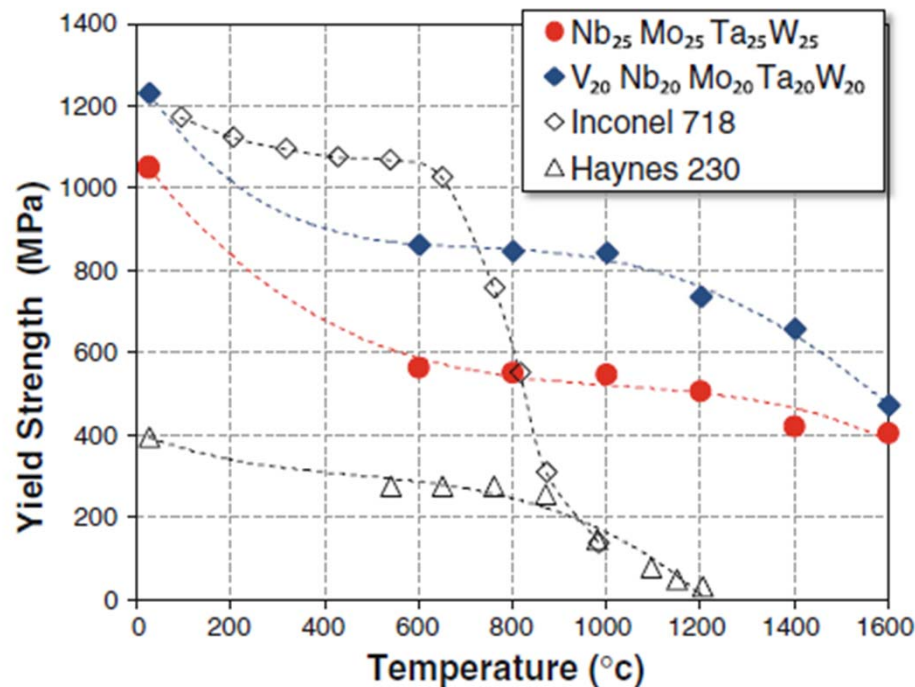
each phase : a multi-element solid solution

→ 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



Inconel 718 : Ni₅₀Cr₁₇Mo_{2.8}Nb_{4.75}

Haynes 230 : Ni₅₇Cr₂₂W₁₄Co₅Mo₂

- 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

Thanks for your kind attention.