Application of metallic foams

A promising candidate of thermal insulation and bio-compatible materials

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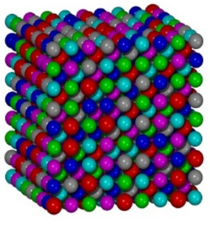
Current status of structural materials on
02APR2018

1. Fabrication of High entropy alloy foams



Introduction of thermal shield material

1) What is the **thermal shield** material ?
2) Needs and problems of **metal matrix thermal shield**

How can we fabricate HEA foam ?

1) **Alloy design** for fabricating HEA foam : Phase separating HEA
2) Fabricating method : **Dealloying process**

What are the advantages of HEA foam ?

1) **Porous structure** of HEA foam
2) **Thermal and Mechanical properties** of HEA foam

➤ **High strength, large ductility and high formability are needed !**

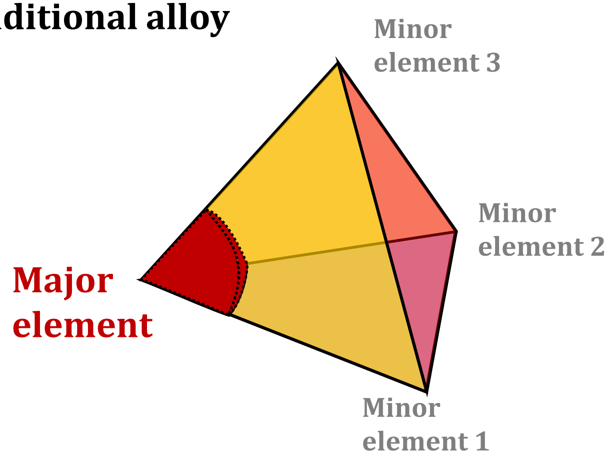
Metallic materials

- **Strong & Ductile**
- **High formability**
- **Heavy**
  Constituted with heavy elements
- **High conductivity**
  Due to the free electrons

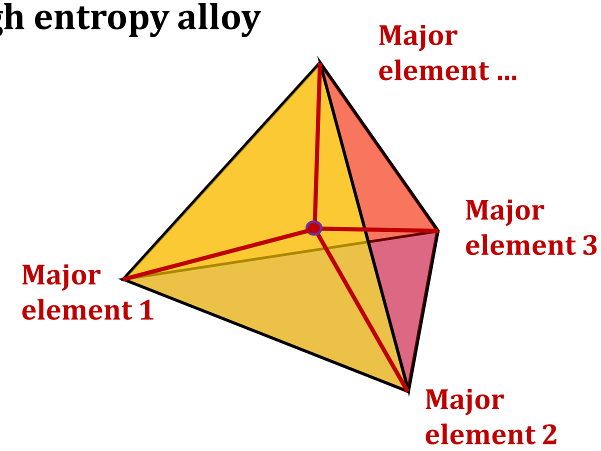
Porous structure

High entropy alloy

Traditional alloy



High entropy alloy



number of elements **↑ ↔ *configurational entropy*** **↑**

$$\Delta S_{config.} = Rln(n)$$

(1) Thermodynamics : high entropy effect

(2) Kinetics : sluggish diffusion effect

(3) Structure : severe lattice distortion effect

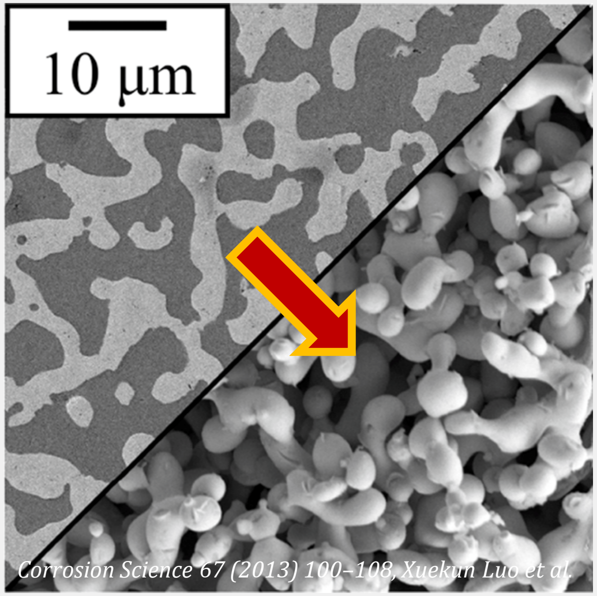
(4) Property : cocktail effect

HEA is stable especially at high temperature

$$\Delta G_{config.} = \Delta H_{config.} - T\Delta S_{config.}$$

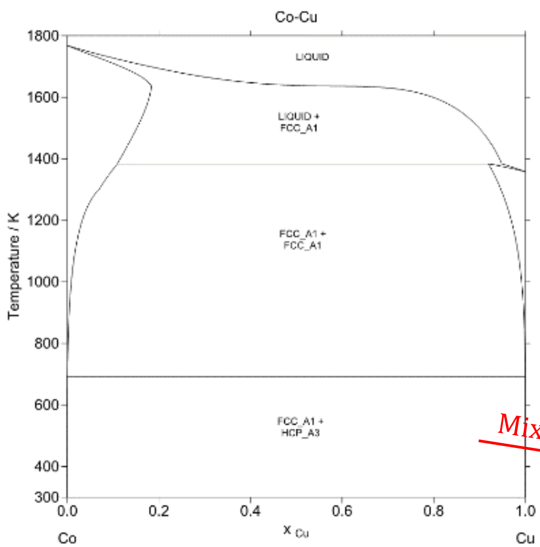
Due to the **high phase stability** and **high melting point** of HEA, it is hard to fabricate foam with conventional methods.

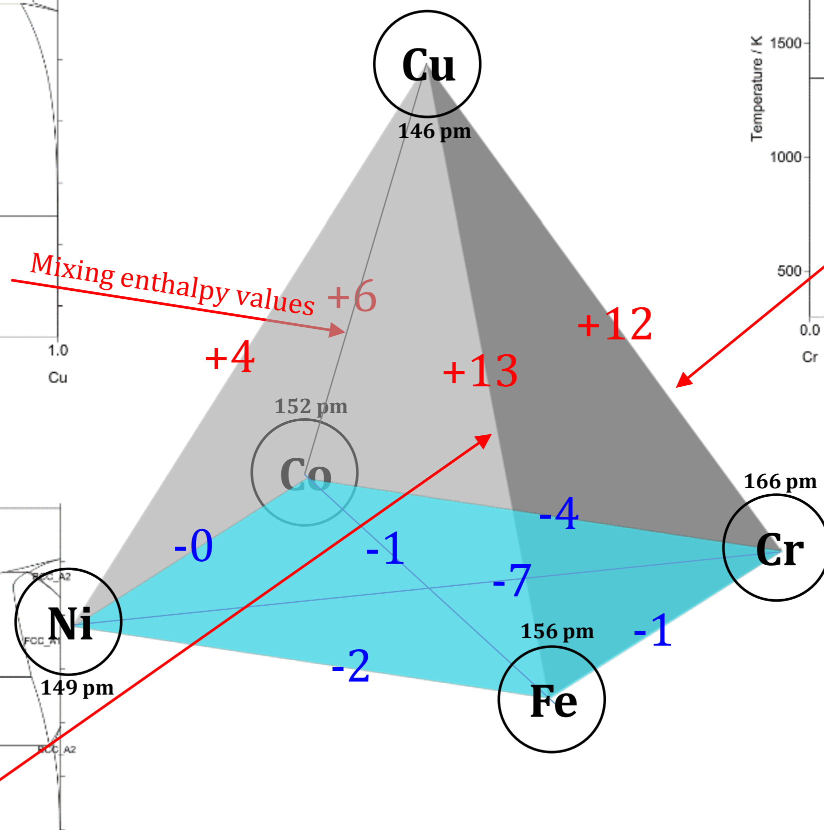
Dealloying process

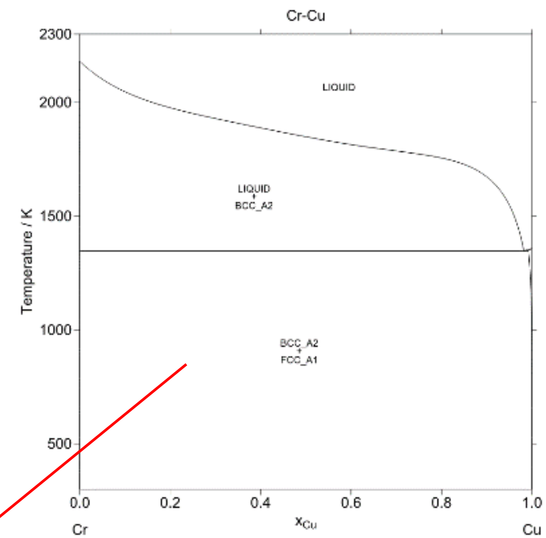


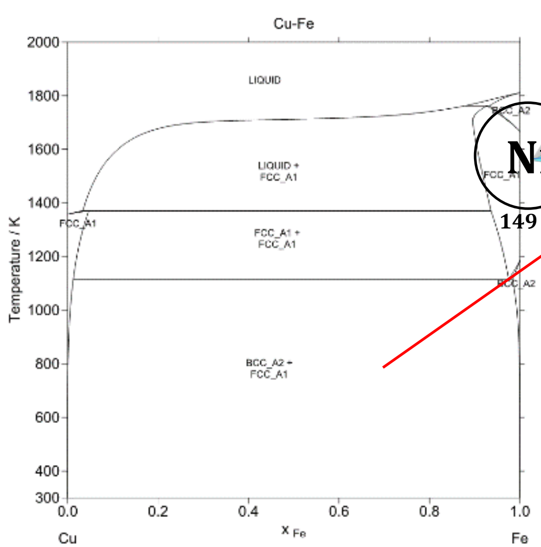
Metal	Index (V)
Most cathodic	
Gold	- 0.00
Copper	-0.35
Iron	-0.85
Zinc	-1.25
Magnesium	-1.85
Most anodic	

is a corrosion type in some solid alloys, when in suitable conditions a component of the alloys is preferentially leached from the material.



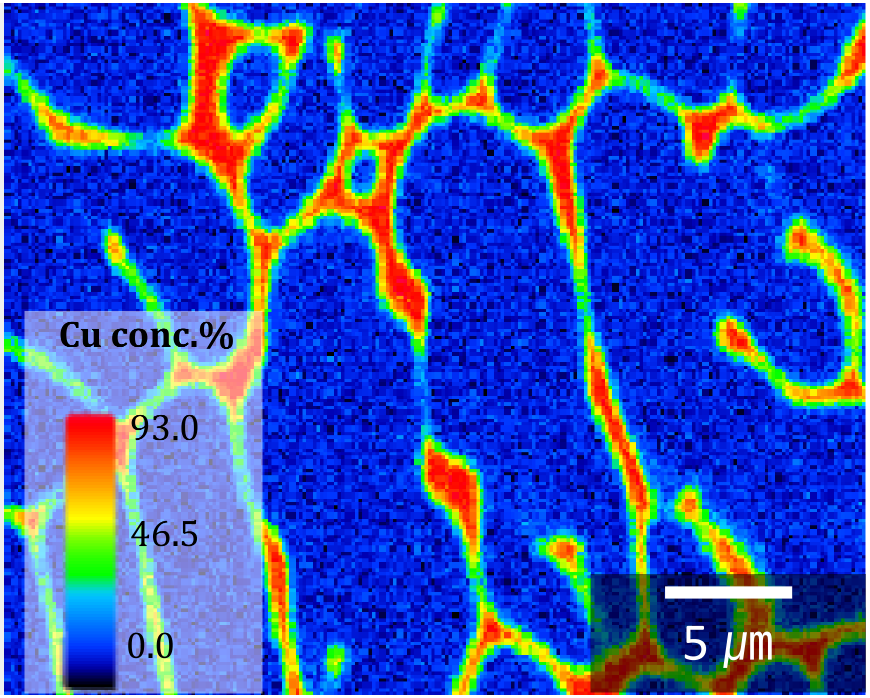






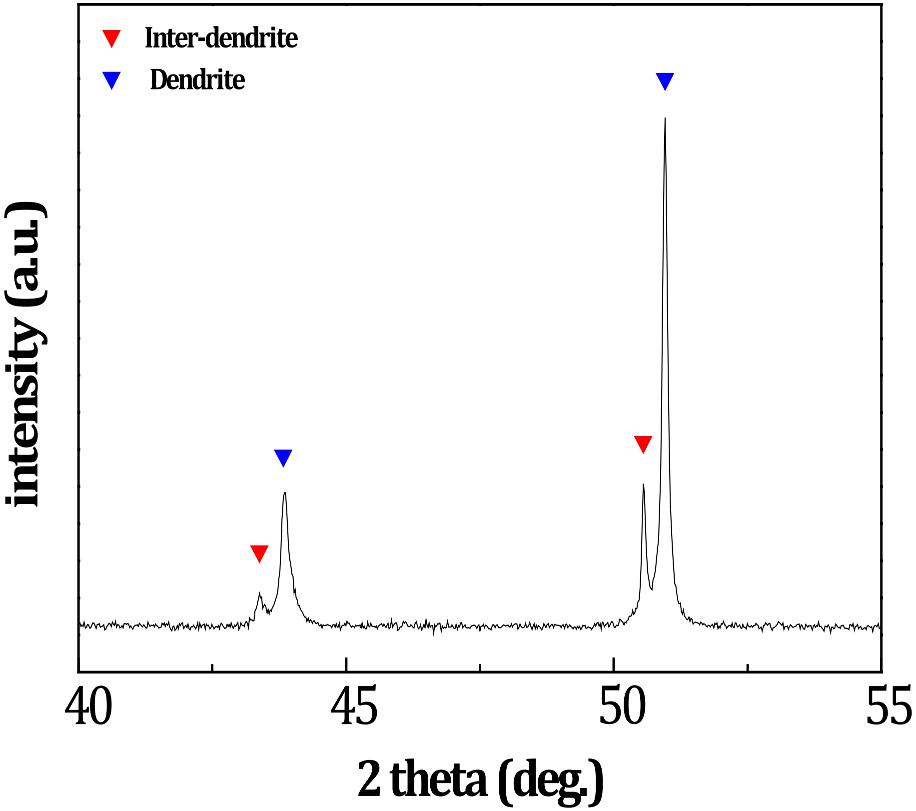
- **Phase separation occurs due to Positive ΔH_{mix} correlation**

1) SEM / EPMA analysis



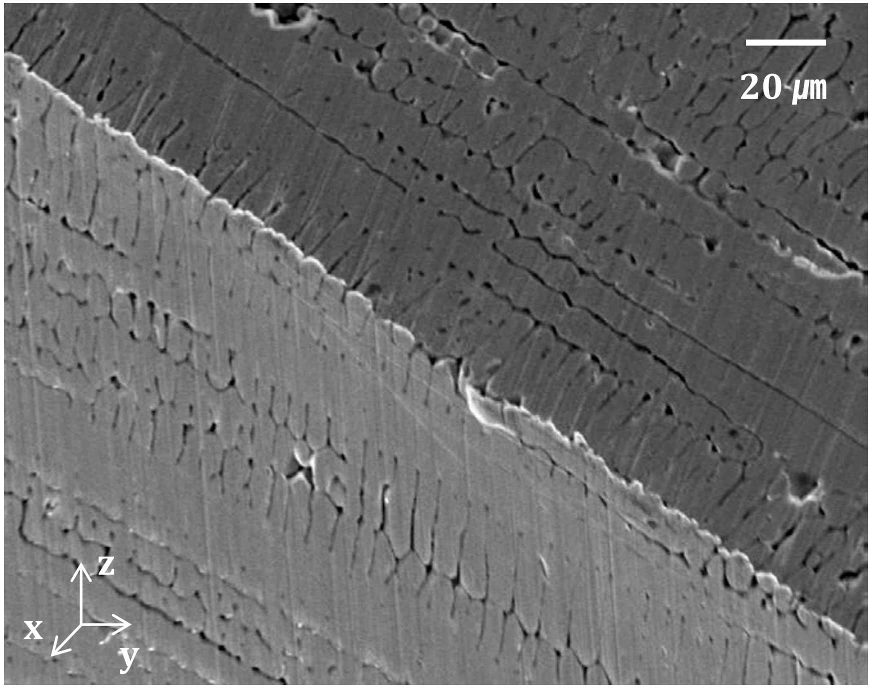
EPMA data	Cu	Fe	Ni	Co	Cr
Inter-dendrite	**84.43**	2.87	6.52	3.38	2.80
Dendrite	**8.31**	22.57	22.05	23.54	23.52

2) XRD pattern

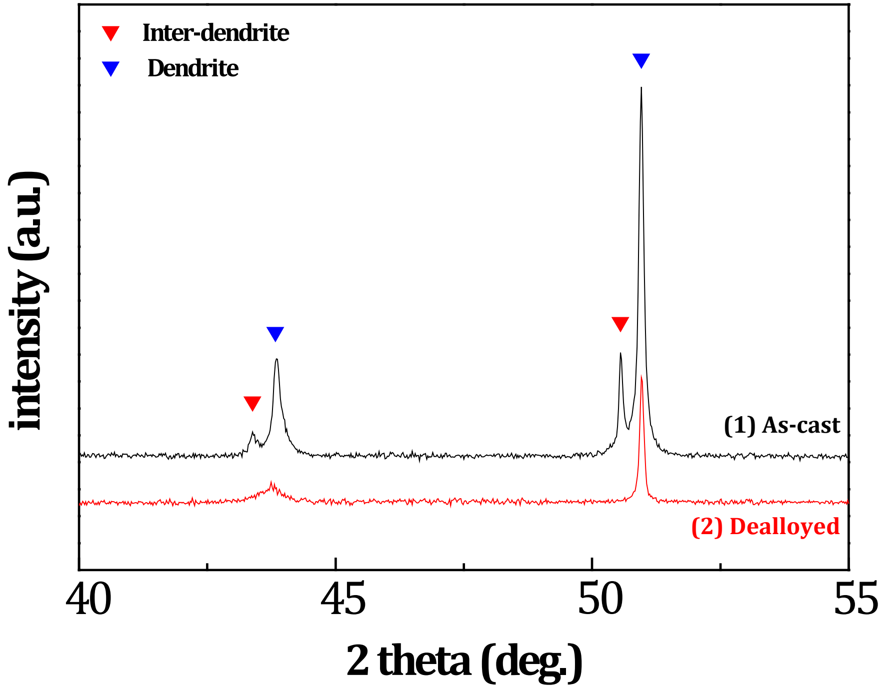


➤ **Cu-rich region is separated even at high entropy condition.**

1) SEM image (tilted 45°)



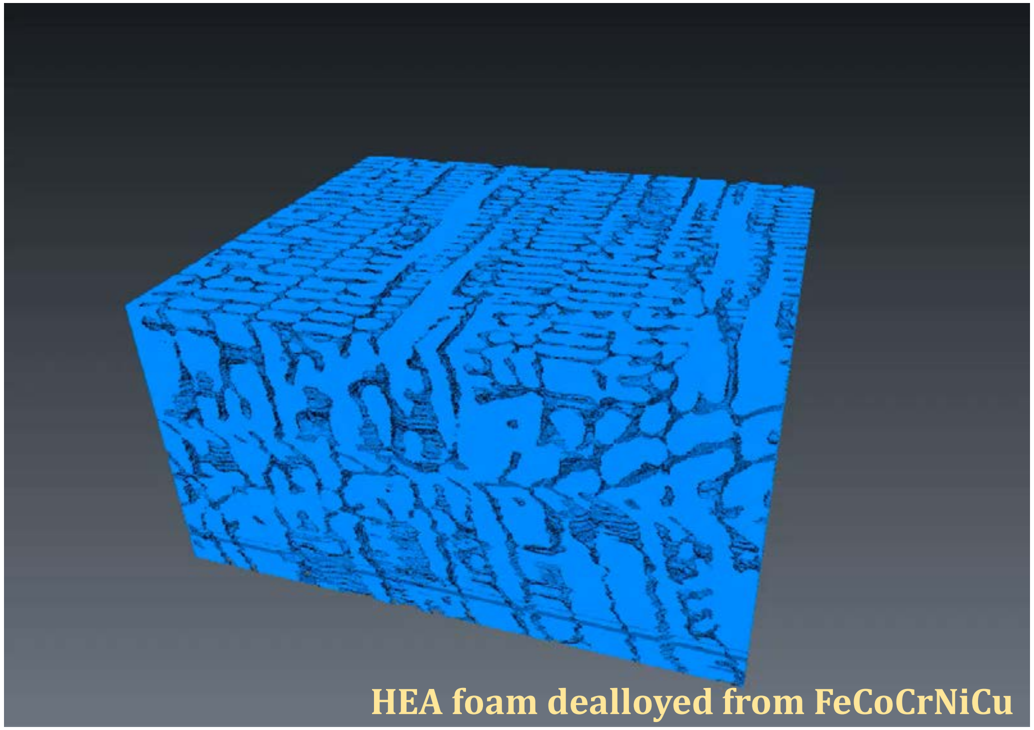
2) XRD pattern

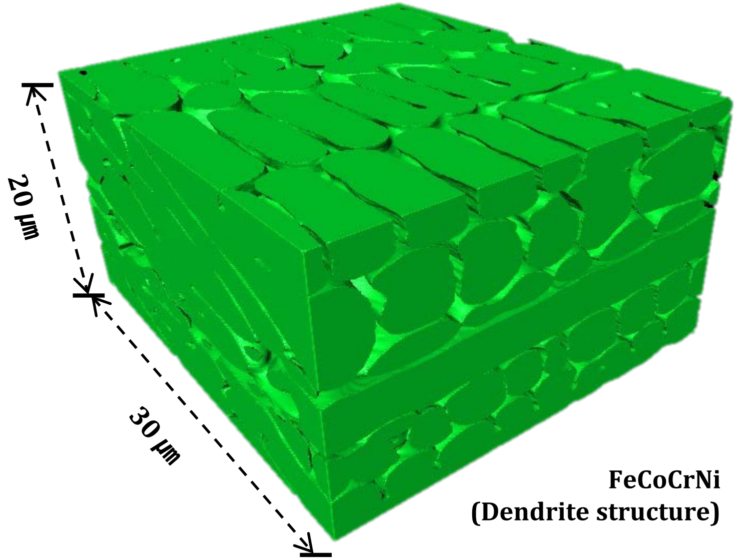


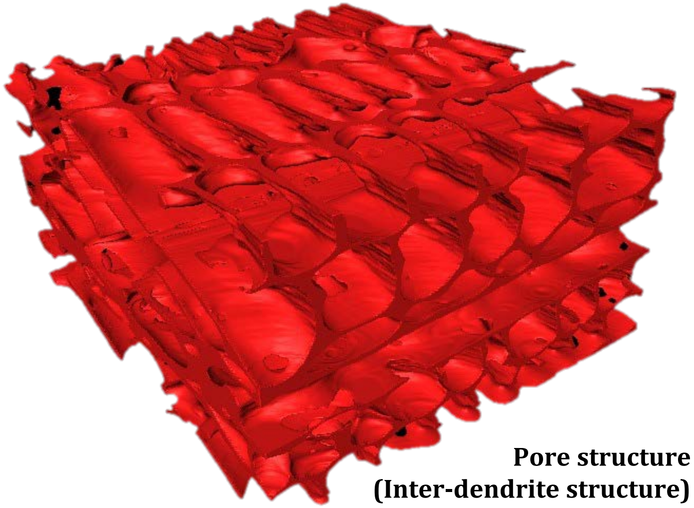
- **Dendritic directional pores are fabricated after dealloying.**

Need to confirm connectivity of pores → **3-D tomography by serial sectioning**

Microstructure confirmation : 3-D tomography

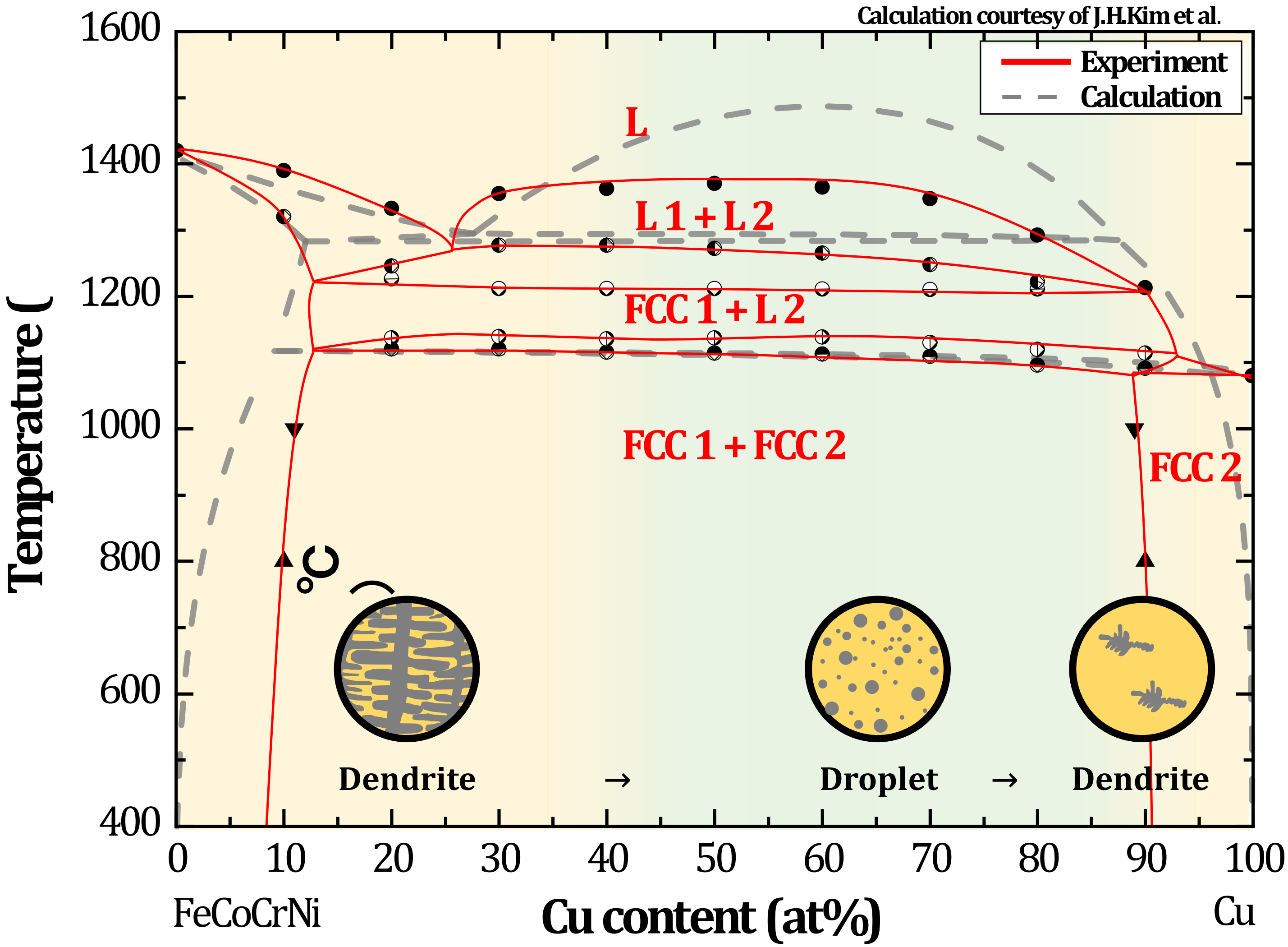






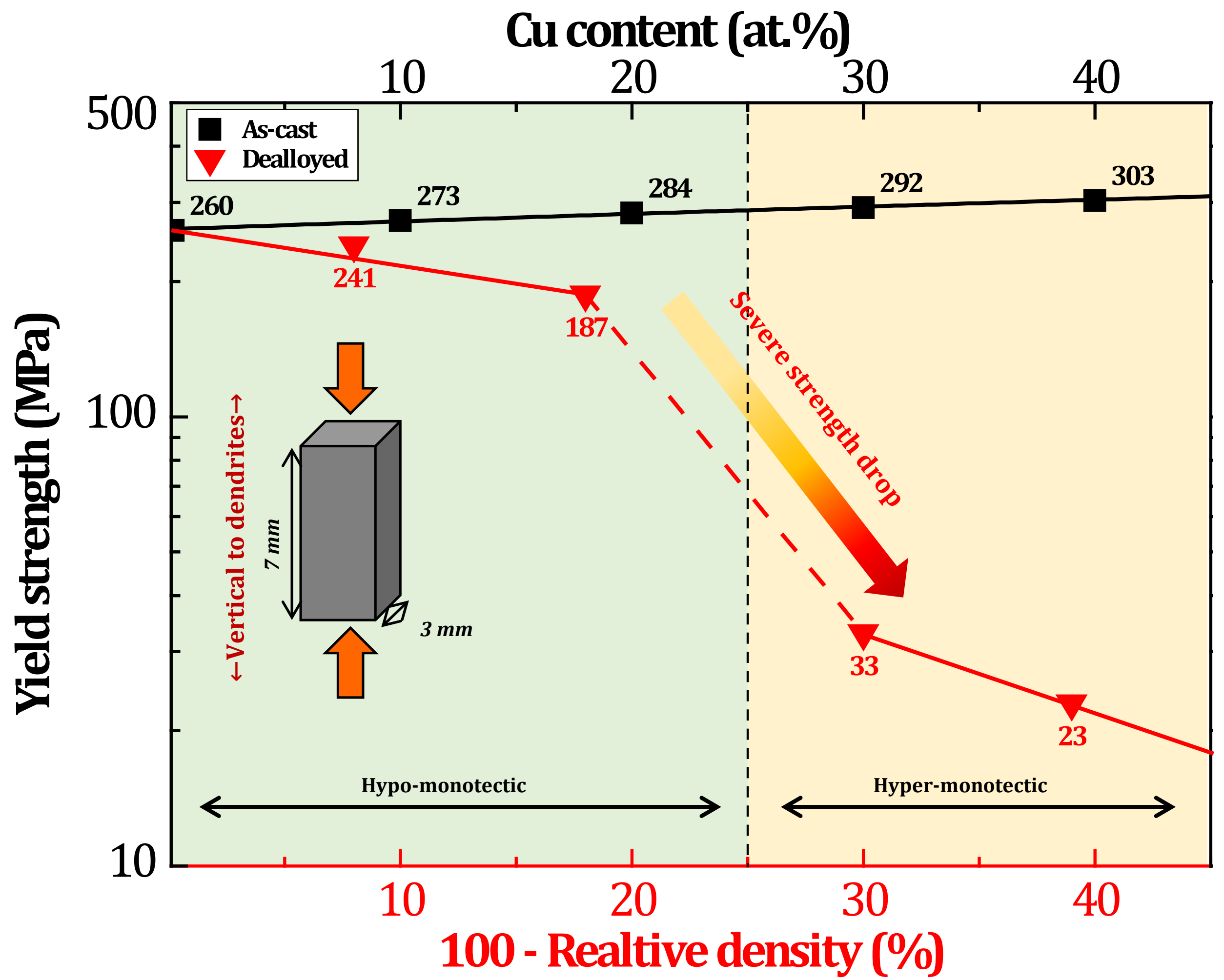
Copper content (at.%)	**10**	**20**	**30**	**40**
Calculated porosity (%)	8.7	18.3	27.6	39.2
Measured porosity (%)	11.1	19.4	29.3	38.5

- ▶ Porosity values are similar between calculated and measured one.
- ▶ The pore structure of interdendrite area is fully **interconnected**.



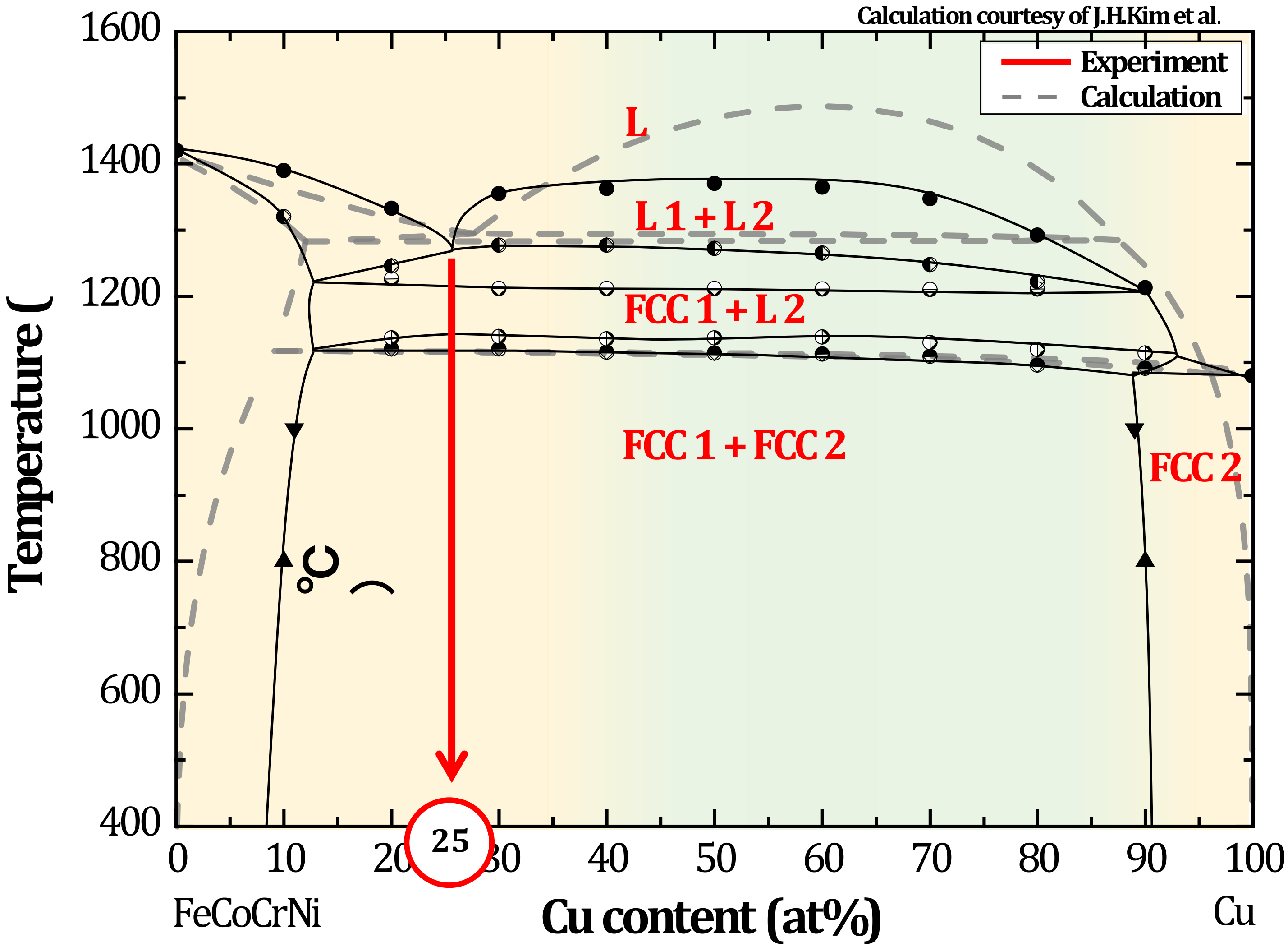
- **Pseudo-binary system between FeCoCrNi and Cu shows monotectic reaction having liquid separation region.**

Compressive yield strength of HEA foam



▶ At low porosity, HEA foam **preserves its yield strength** which was about 200 MPa.

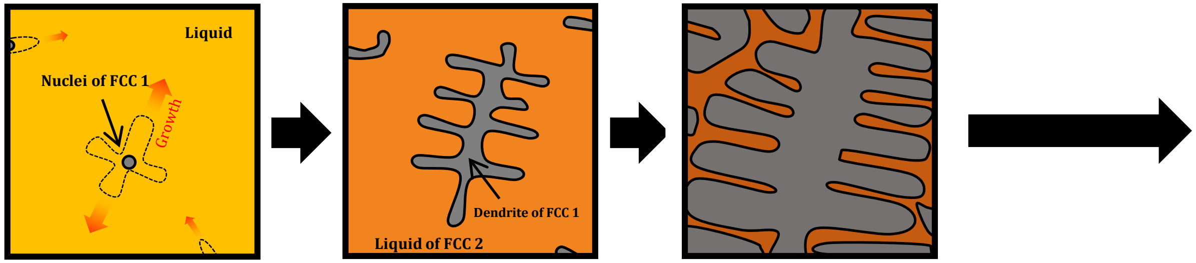
▶ However, after about 25 % of Cu content, the **yield strength drops severely**.



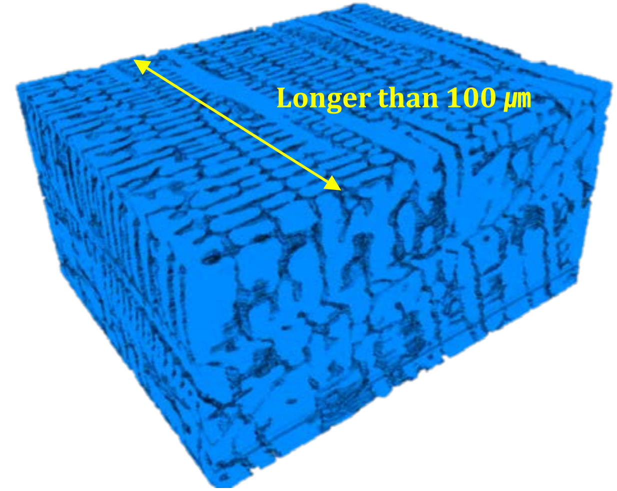
- Pseudo-binary system between FeCoCrNi and Cu shows **monotectic reaction** having liquid separation region.

Strength drop due to monotectic reaction

a) Hypo-monotectic reaction (20 at.% of Cu)



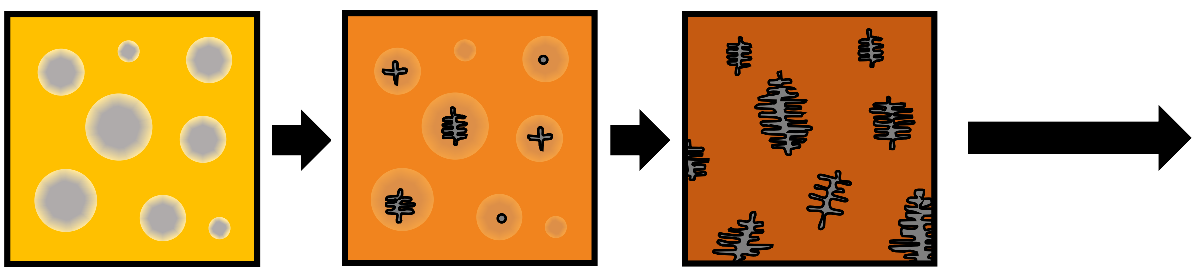
Nucleation of FCC 1 | Dendritic growth of FCC 1 | Thick & Long dendrites



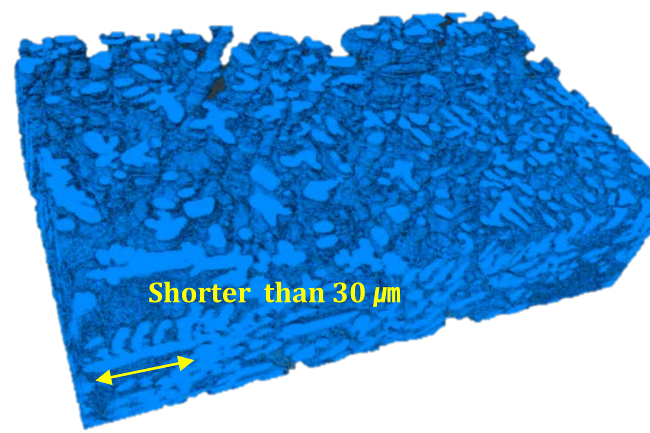
Dendrites of hypo-monotectic condition are **interconnected** well.

➡ **High strength**

b) Hyper-monotectic reaction (40 at.% of Cu)

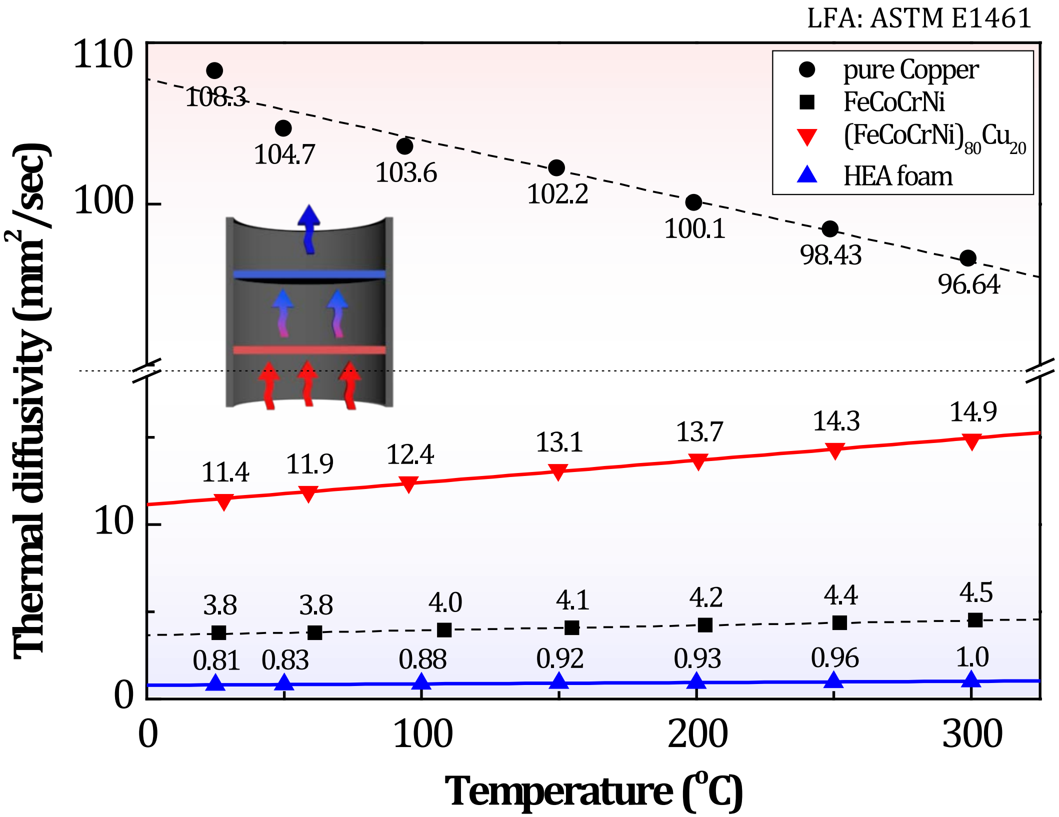


Liquid phase separation | Dendritic growth of FCC 1 | Thin and short dendrites



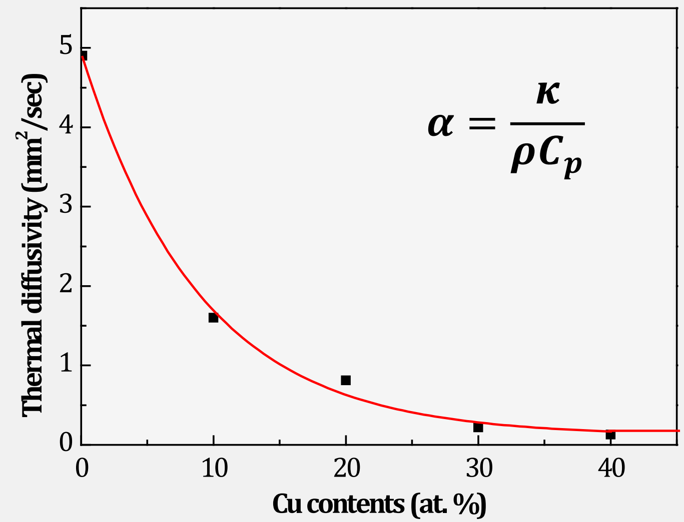
Each small dendrite is **separated in short period**, since each of it is nucleated after liquid separation.

➡ **Low strength**



Cu contents (%)	0	10	20	30	40
Thermal cond.	15.4	5.1	2.6	0.68	0.35
Thermal diff.	4.9	1.6	0.81	0.22	0.13

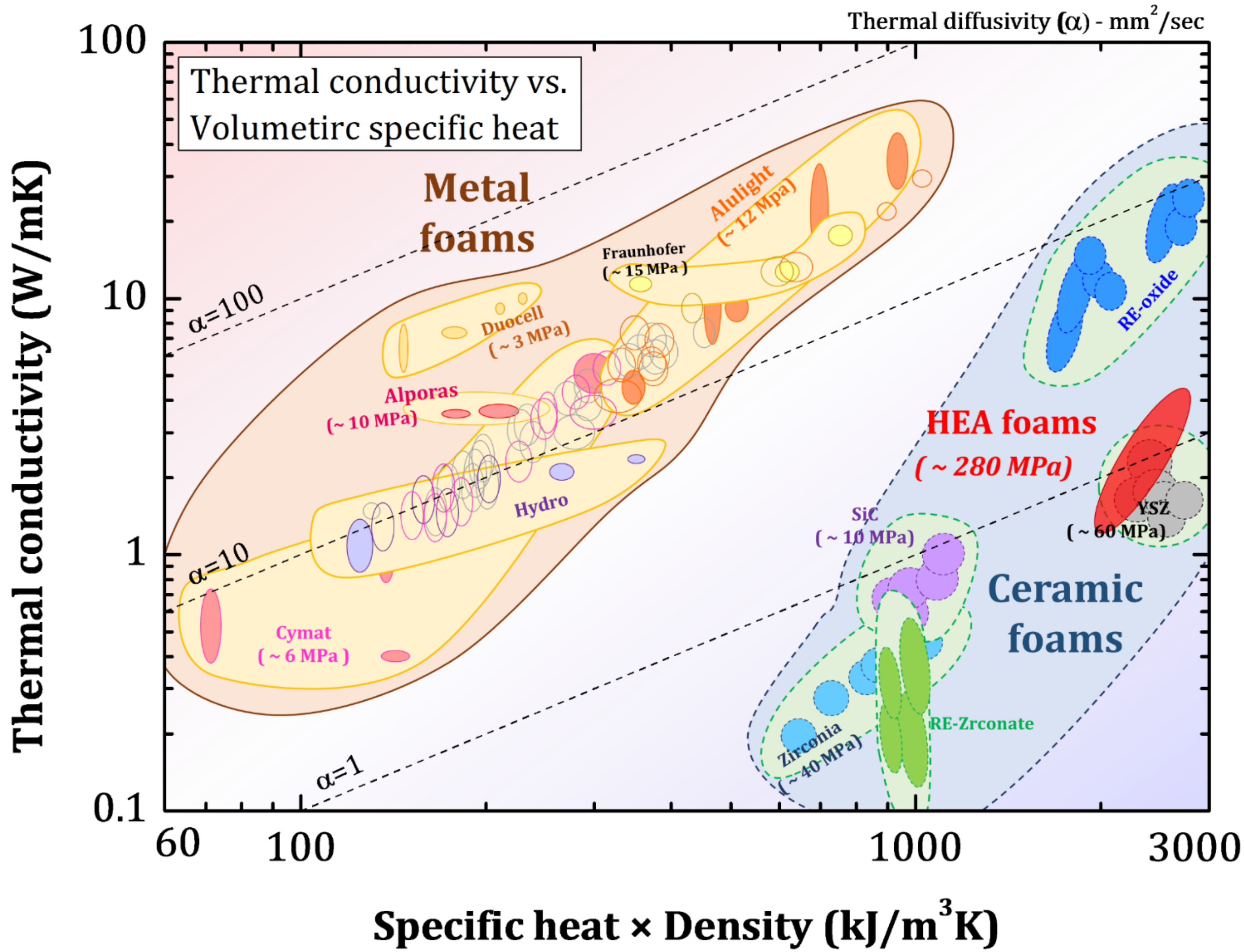
➤ **Thermal diffusivity decreases exponentially against the composition of Cu which is proportional to porosity.**



$$\alpha = \frac{\kappa}{\rho C_p}$$

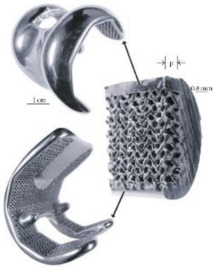
300 K, 1atm

Material	α(mm²/s)
Carbon	**216.5**
Silver	165.63
Copper	**111**
Molybdenum	54.3
Air	19
Steel, 1% C	11.72
Quartz	1.4
Sandstone	1.15
Brick, common	**0.52**
Glass, window	**0.34**
HEA foam	**0.1 ~ 5**
Rubber	0.089 - 0.13
Wood	0.082



➤ **HEA foam shows similar thermal diffusivity value with ceramic foams**

2. Fabrication of Biocompatible Co-Cr foams

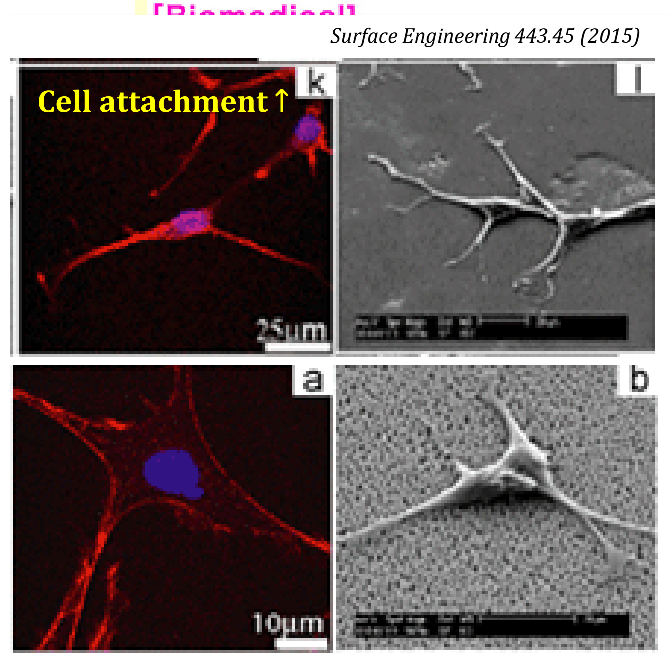


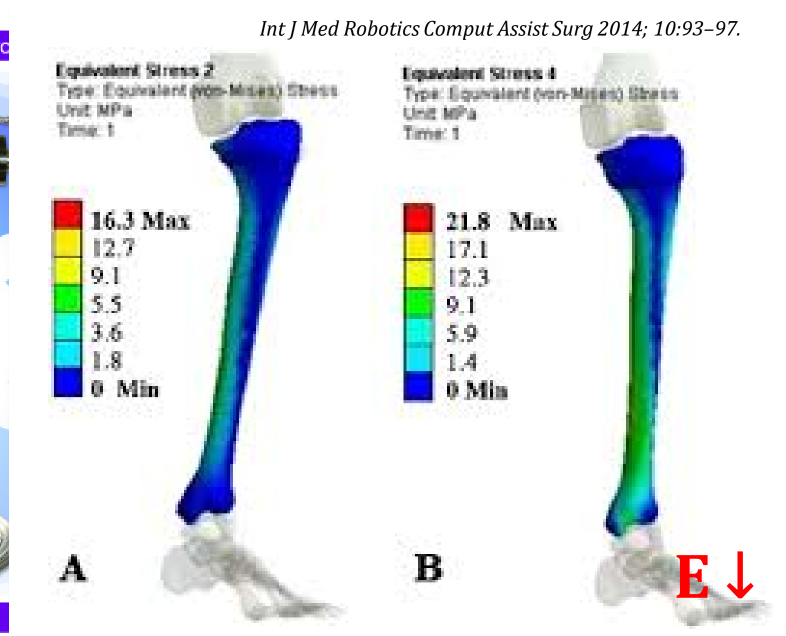
Fabrication of porous Co-Cr alloy by LMD process

- Introduction of bio-compatible **Co-Cr alloy**
- Fabrication method : Liquid metal dealloying process, **LMD**
- Microstructure **optimization** - Process condition control

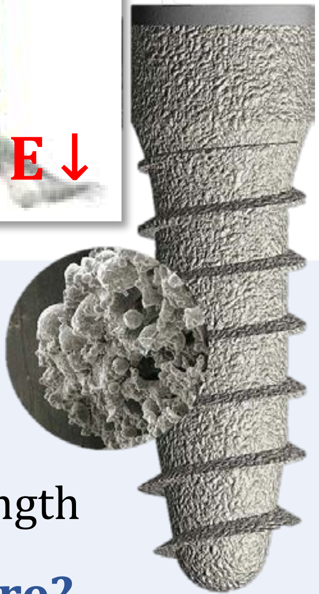
Properties of Co-Cr alloy foams

- **Biocompatibility**
  - Hydrophilic test : Water drop test
  - Osteoblast cultivation on Co-Cr alloy foam
- **Mechanical properties**
  - Compressive properties of Co-Cr alloy foam





-Cr alloy

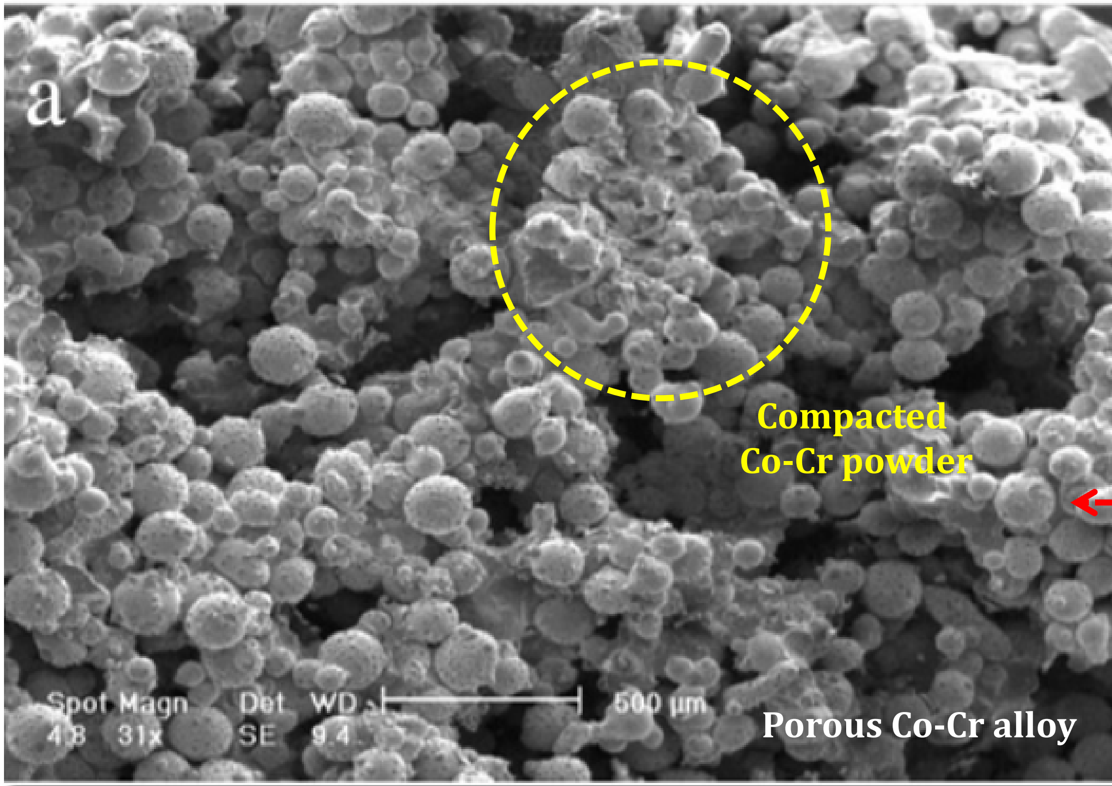


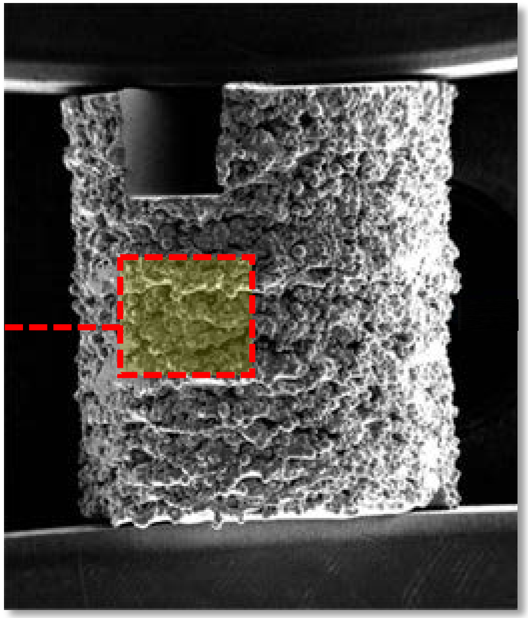
- ✓ Excellent **bio-compatibility**
- ✓ High **corrosion and fatigue resistance**
- ✓ **Good mechanical properties -** fracture toughness and strength

+ Porous structure?

➤ **Porous Co-Cr alloy can be a good candidate for implant materials**

M.T. Dehaghani et al. / Materials and Design 88 (2015) 406–413





✓ **Porous Co-Cr alloy is normally fabricated by sintering powder**

- It is **hard to control property** of porous structure with sintering technique - **Connectivity**
- A material developed by sintering is normally **exhibiting brittleness** due to defects

➤ **New method to fabricate porous structure of Co-Cr alloy is needed !**

Dealloying by metallic melt

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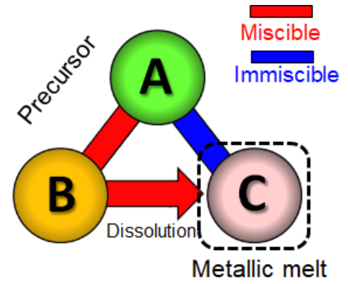

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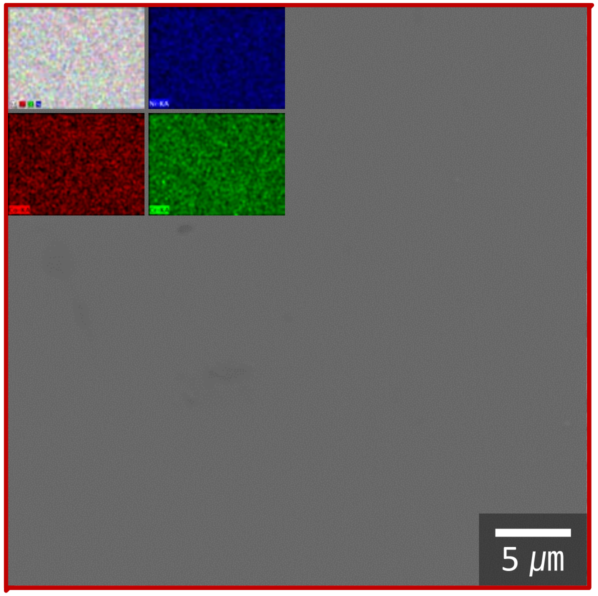
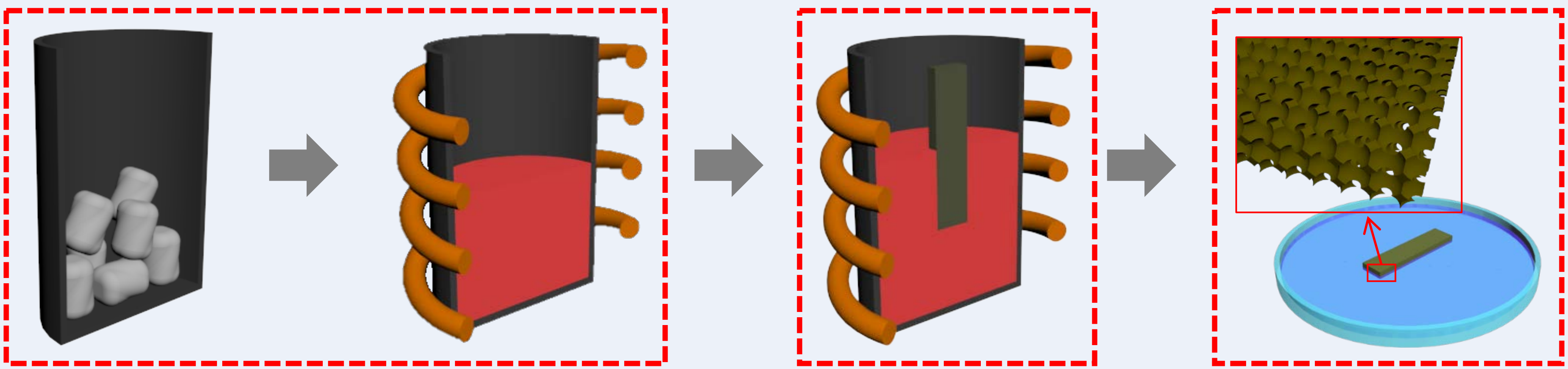
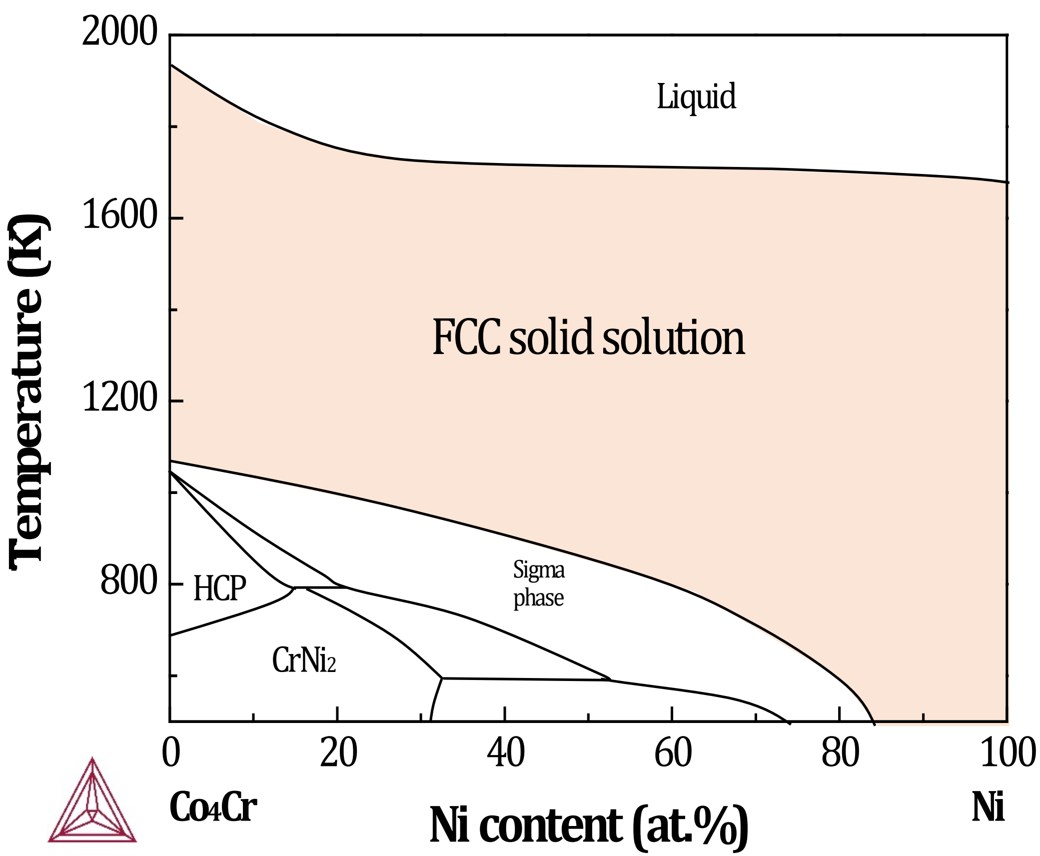
ABSTRACT

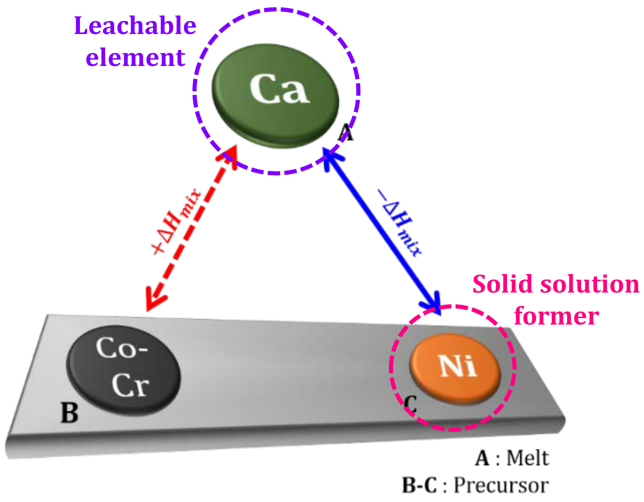
Dealloying, which commonly involves corrosion processes in aqueous solutions, is a promising technique for preparing functional nanoporous metals. While this technique is ideal for preparing nanoporous noble metals such as of Au, it is not readily applicable to less-noble metals. Here, we propose a novel dealloying method employing a metallic melt, instead of an aqueous solution, as the dealloying liquid for a preparing of nanoporous metals. An atomic interaction among alloy components and metallic melt causes specific component to dissolve out from the alloy solid into the melt with self-organizing nanoporous structure by the remaining component. The dealloying method can be applied for preparation of nanoporous less-noble metal such as of Ti for the development of functional materials such as fluid filters, gas absorption media, and biomaterials.





Metallic materials can be dealloyed by a liquid metal as well as an etchant



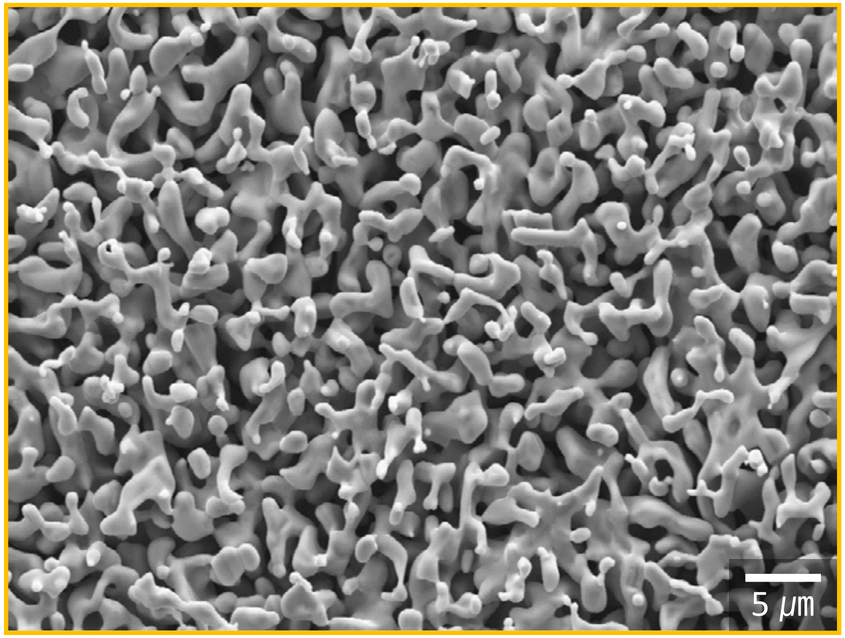


	Ca	Ni	Co	Cr
Ca	0	-7	+2	+38
Ni	-	0	-1	-7
Co	-	-	0	-4
Cr	-	-	-	0

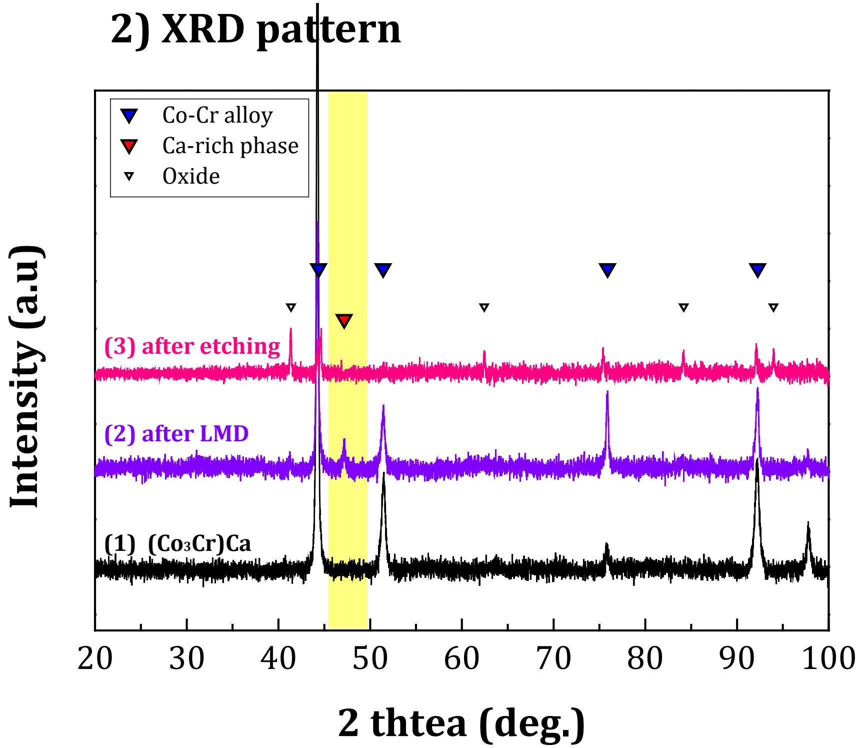
- ✓ To obtain target composition which is Co_3Cr, precursor was prepared with composition of **Co_4Cr-Ni.**
- ✓ The precursor alloy was **ternary single solid solution** of cobalt, chromium and nickel.

Ternary alloy was designed with consideration of thermodynamic correlation

1) SEM image



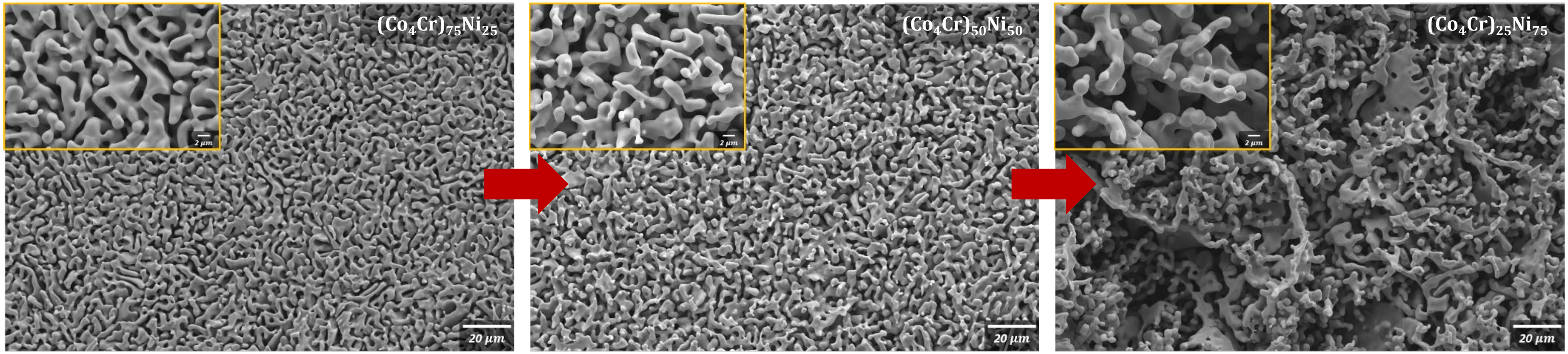
2) XRD pattern



- ✓ The precursor alloy, $Co_{40}Cr_{10}$**Ni_{50}**, was immersed in **1000°C Ca melt for 10 minutes**
- ✓ After LMD process, **well-connected Ca rich phase** was formed in several mm depth
- ✓ Etched in 0.3M nitric acid, the Ca-rich phase disappeared and only Co-Cr alloy phase remains

Porous Co-Cr alloy was successfully fabricated by LMD process

Porosity control by changing precursor composition



	Co	Cr	Ni	Ca
Content (at.%)	68.79	25.79	5.42	0.00

Relative density : **0.784**

	Co	Cr	Ni	Ca
Content (at.%)	68.47	24.30	6.89	0.34

Relative density : **0.561**

	Co	Cr	Ni	Ca
Content (at.%)	66.57	25.77	7.65	0.00

Relative density : **0.320**

- ✓ **The porosity was successfully controlled by changing Ni content**
  - which has negative enthalpy of mixing with Ca.
- ✓ **Very small amount of Ni is still remaining in Co-Cr alloy foam.**
  - Because Ni has solubility limit, 7at.%, to Co-Cr alloy, small amount of Ni can be remained.
  - And the ratio between Co and Cr was changed to 3:1 after LMD process

It is possible to control porosity by changing composition of precursor

Free energy of dealloying

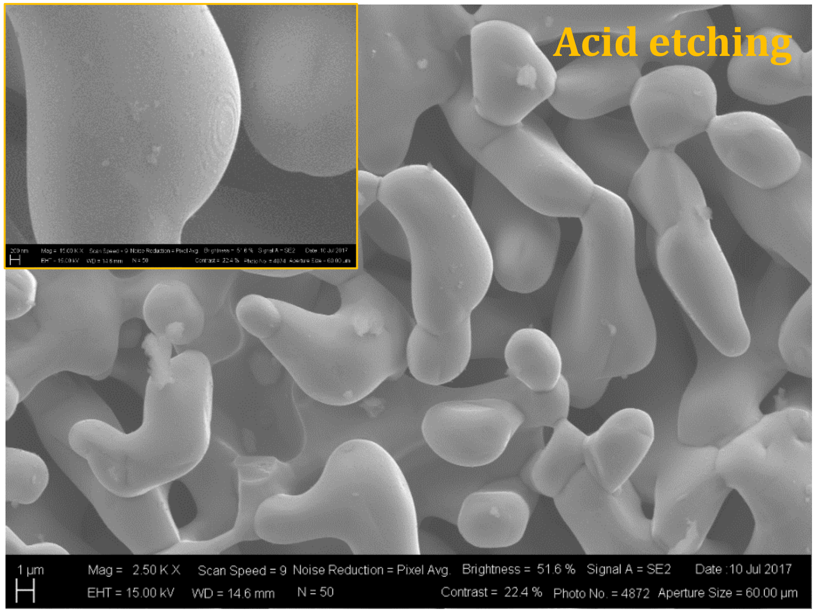
$$F = \alpha\, c(1-c) + \boxed{K \cdot T[c\ln c + (1-c)\ln(1-c)]}$$

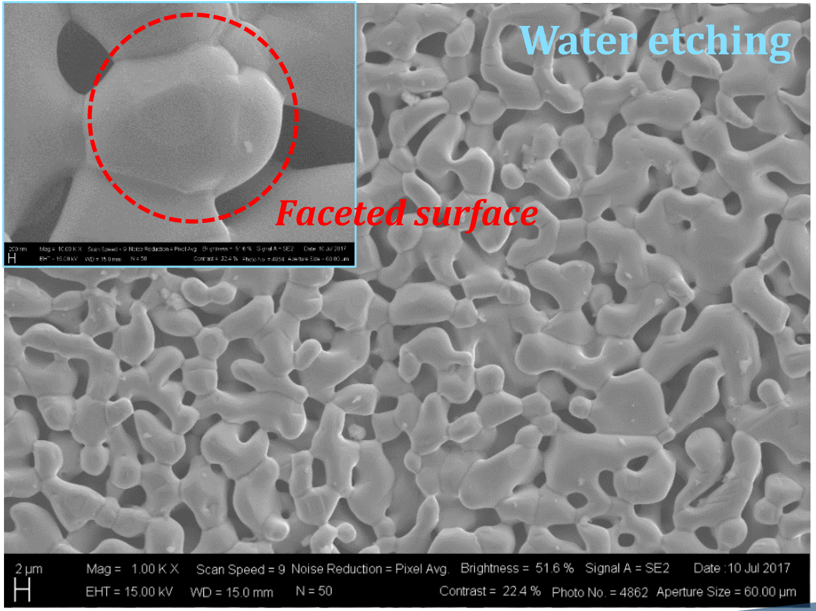
$$\alpha = 6(E_{a\text{-}b} - (1/2)(E_{a\text{-}a} + E_{b\text{-}b}))$$

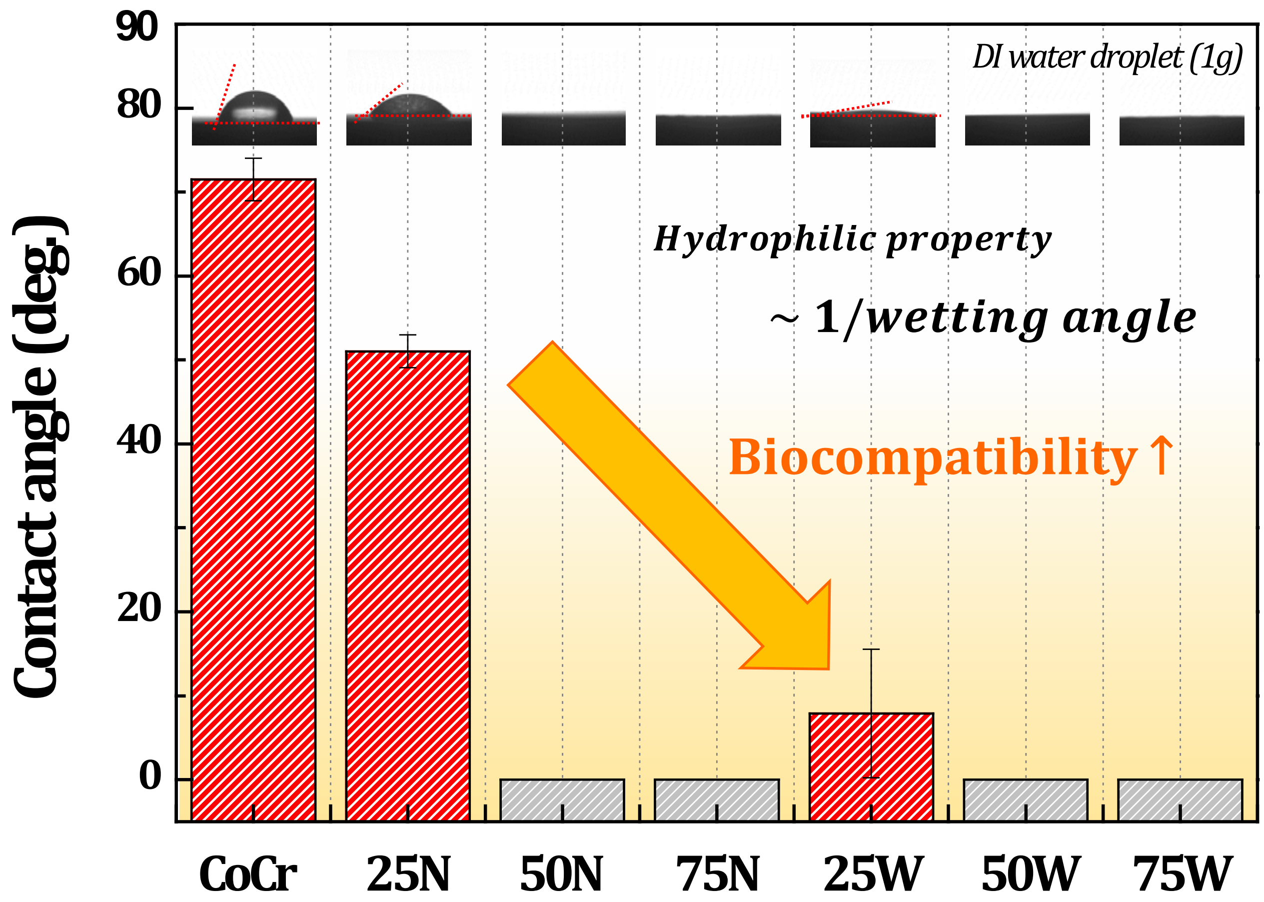
$$K_\alpha = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

- $Ca + 2\ H_2O = Ca(OH)_2 + H_2$
  - ▶ $K_{\alpha,H2O} = 10^{-14}$: **Meaningless value**
- $4\ Ca + 10\ HNO_3 = 4\ Ca(NO_3)_2 + N_2O + 5\ H_2O$
  - ▶ $K_{\alpha,H2O} = 20$: **Considerable influence**

Etchant can affect surface morphology of Co-Cr alloy foam



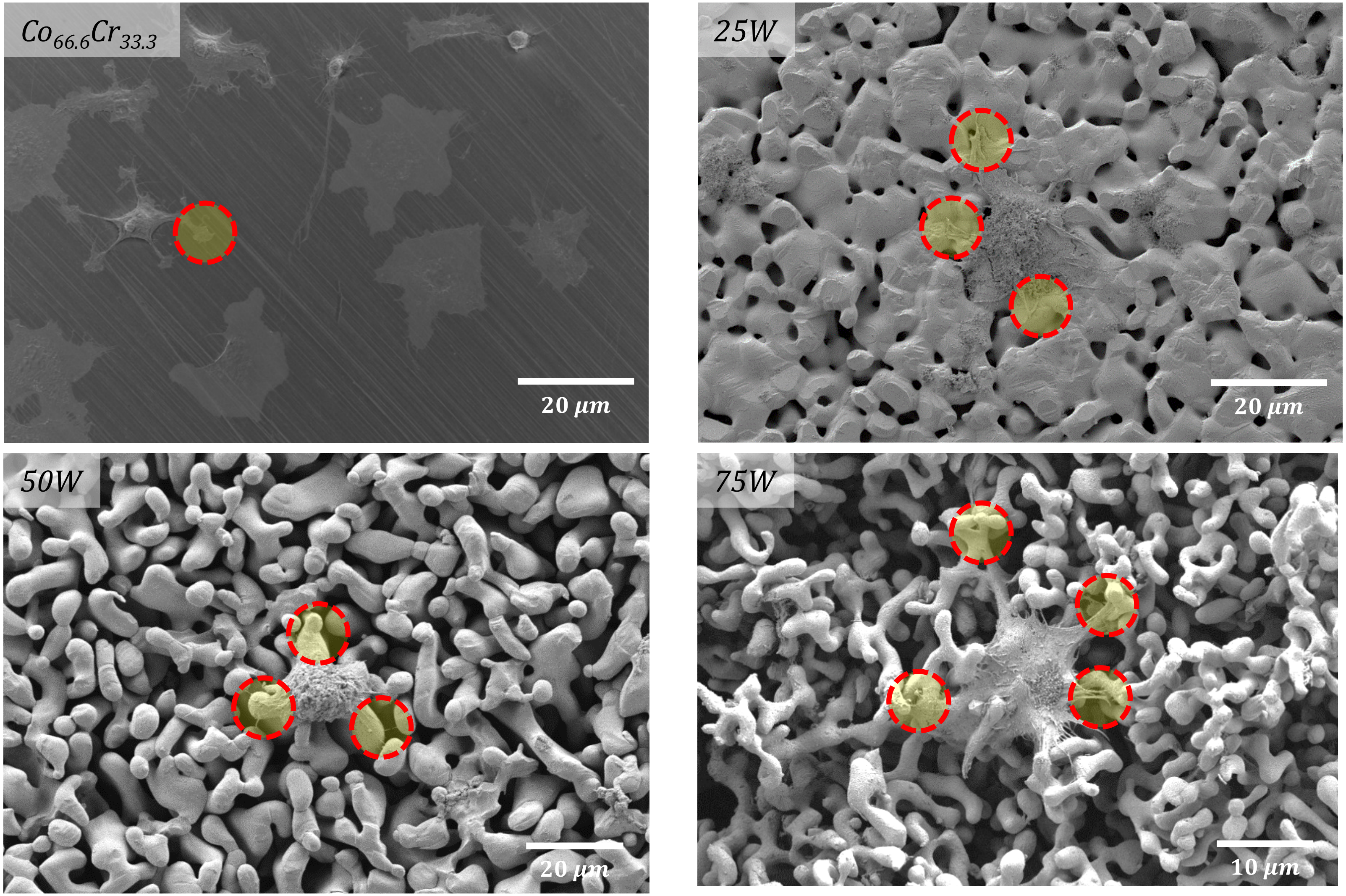




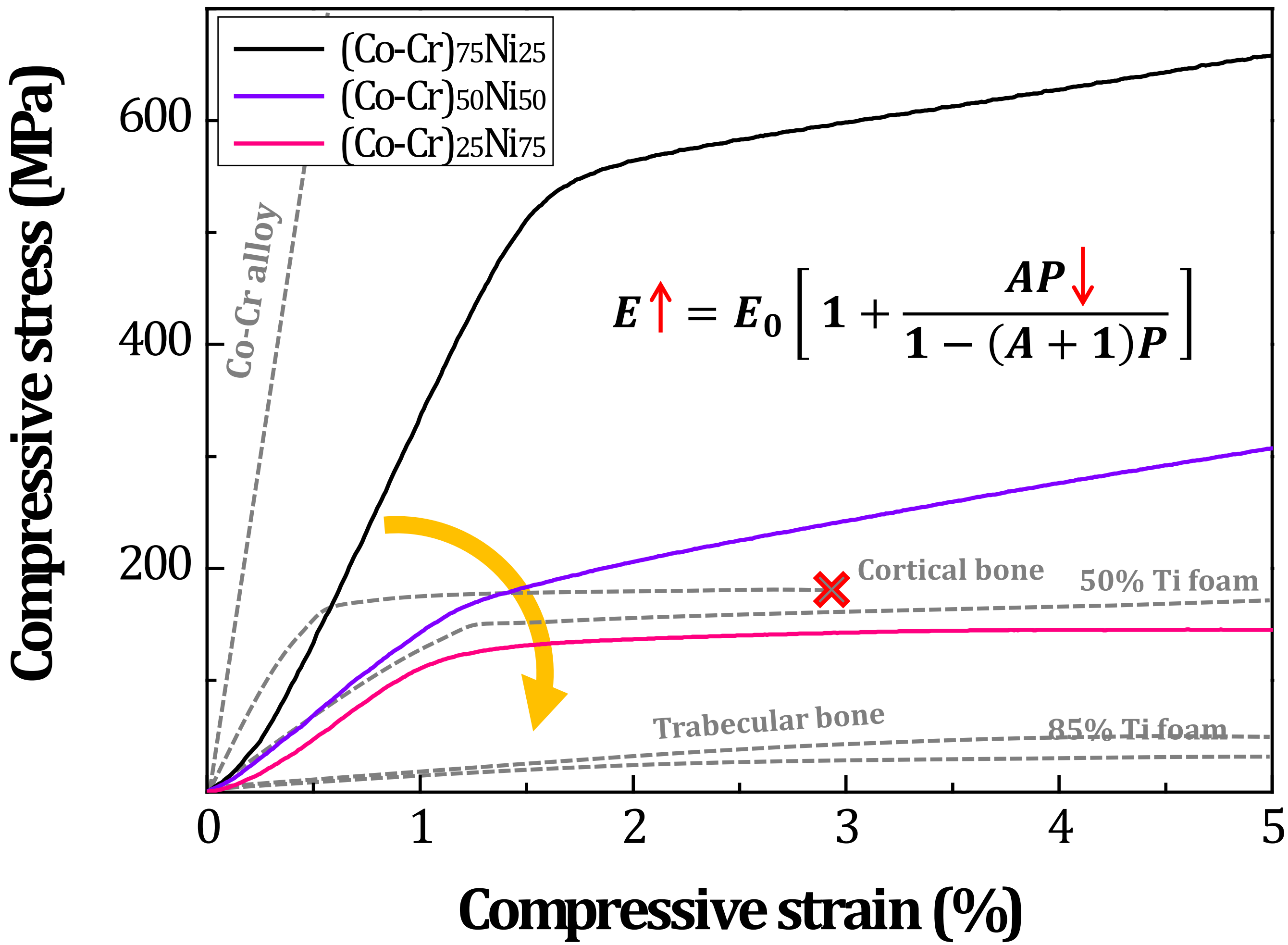
- ✓ **Every foam is more hydrophilic than Co-Cr alloy because of its porous structure**
  - This is because of not only intrinsic property of Co-Cr alloy but also the porous structure

➤ **Biocompatibility can be enhanced by surface morphology of porous structure**

Osteoblast cultivation on Co-Cr alloy foams



- ✓ Co-Cr alloy shows very high **bio-compatibility itself** – Several cells are well-attached on the surface
- ✓ Every sample with various porosity **shows good bio-compatibility** which is similar to Co-Cr alloy



- ✓ **Elastic modulus** of Co-Cr alloy foam **decreased** according to increase of porosity
- ✓ **Compressive strength** of Co-Cr alloy foam was **enough high** by comparison with Ti alloy foam

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