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Phase Formation Rules for High Entropy Alloys

Yong Zhang

University of Science and Technology Beijing

ICAMP5

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Prof. Hywel A Davies;
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Outlines

I. Background & Motivations

II. Results & Discussions

III. Summaries

I. Background & Motivations

1.1 Alloys Design Strategy

(1) Conventional alloys

Alloy=A+δB+ δC+;
A>50%; …

Steel, A=Fe,
B=Carbon, δB<2%;

Cast Iron, A=Fe,
B=Carbon, δB<6.5%

(2) High Entropy Alloys

HEAs=A+B+C+D+E; 50%<A\B\C\D\E>15%

FCC type HEA Solid Solution

CoCrCuFeNi=HEA,

Yeh, MMTA, 2004;

BCC type HEA Solid Solution

AlCoCrFeNi=HEA ,

Zhou, APL, 2007

Al_{20}[TiVMnHEA]$_{80}$,

Zhou, MSEA, 2007

1.2 Thermodynamically

$$S = X_A S_A + X_B S_B + \Delta S_{mix}$$

For the regular solution:

$$\Delta S_{mix} = -R(X_A LnX_A + X_B LnX_B)$$

$$S = X_A S_A + X_B S_B$$

Solid solution has higher entropy than the mechanical mixture does.

Gibbs Free Energy

G_A G_B

G_{AB}

$$\Delta G_{mix} = G_{AB} - (X_A G_A + X_B G_B)$$

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

1.3 Properties and Applications

Properties

1. High Strength; *Zhou, APL, 2007;*
2. High wear resistance; *Lin, Surface Coating technology, 2008.*
3. High corrosion resistance; *Lee, Thin Solid Films, 2008;*
4. High thermo-stability; *Tsai, APL, 2008.*

Potential Applications

1 Coatings, Barriers, etc.

Diffusion barriers for Cu interconnections; *Tsai, APL, 2008*

2 Structural Materials

3 Energy Storage Materials,

Raju, Journal of power Sources, 2008;

4 Molds

1.4 Motivations

To understand what is the dominant factors for the phase formation of the HEAs

1 Atomic radius, or atomic volume;

Atomic Radius

The contents of Al, Ti, Cu, Co in the HEAs were changed

$$\delta = \sqrt{\sum_{i=1}^{N} c_i (1 - r_i / \bar{r})^2}$$

$$\bar{r} = \sum_{i=1}^{N} C_i r_i$$

Kittel, Introduction to Solid State Physics

2 Enthalpy of Mixing;

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{N} \Omega_{ij} c_i c_j$$

3 Entropy of Mixing

$$\Delta S_{mix} = -R \sum_{i=1}^{N} C_i Ln C_i$$

4 Cooling Rate

Critical cooling rate? Like the BMG?

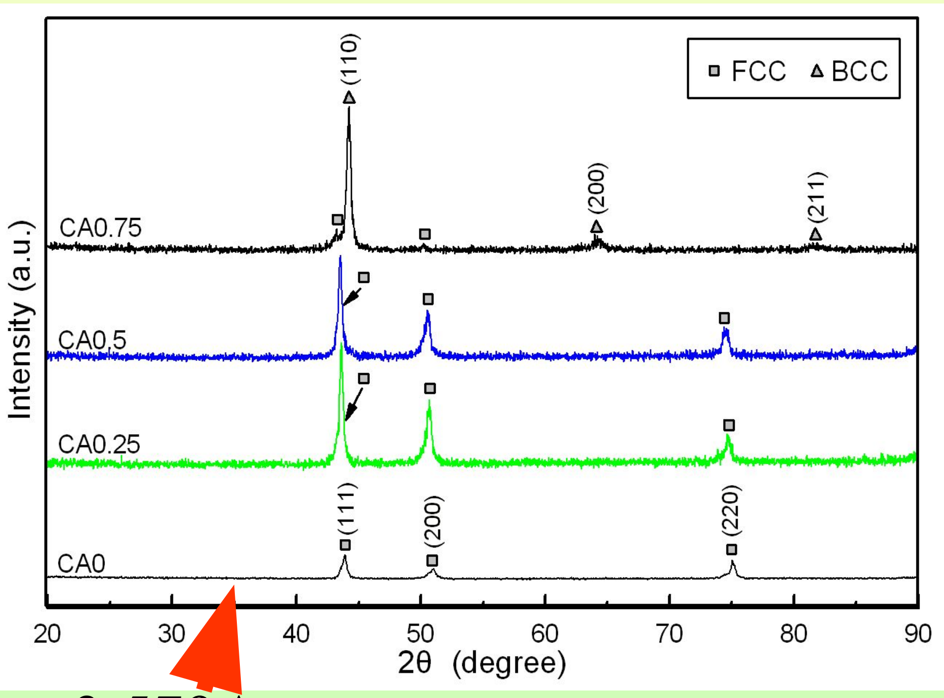
5 Tensile and compressive properties

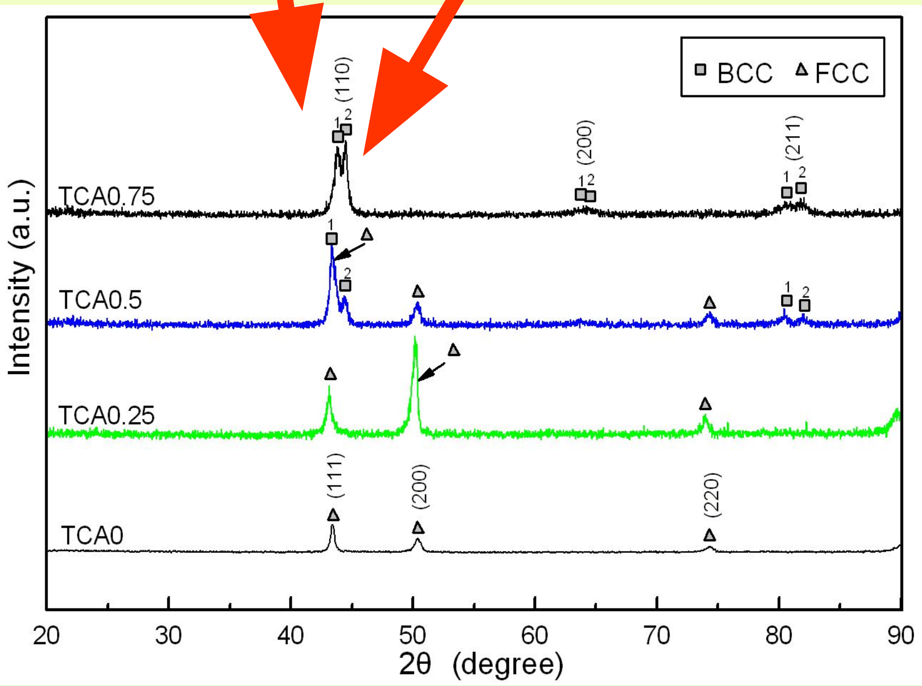
Tensile elongation=0? Like BMG?

II. Results & Discussions

2.1. Alloying with different atomic size, Al, Cu, Co, Ti

Al=1.438A (y=0, 0.25, 0.5, 0.75) 2.913A,2.872A



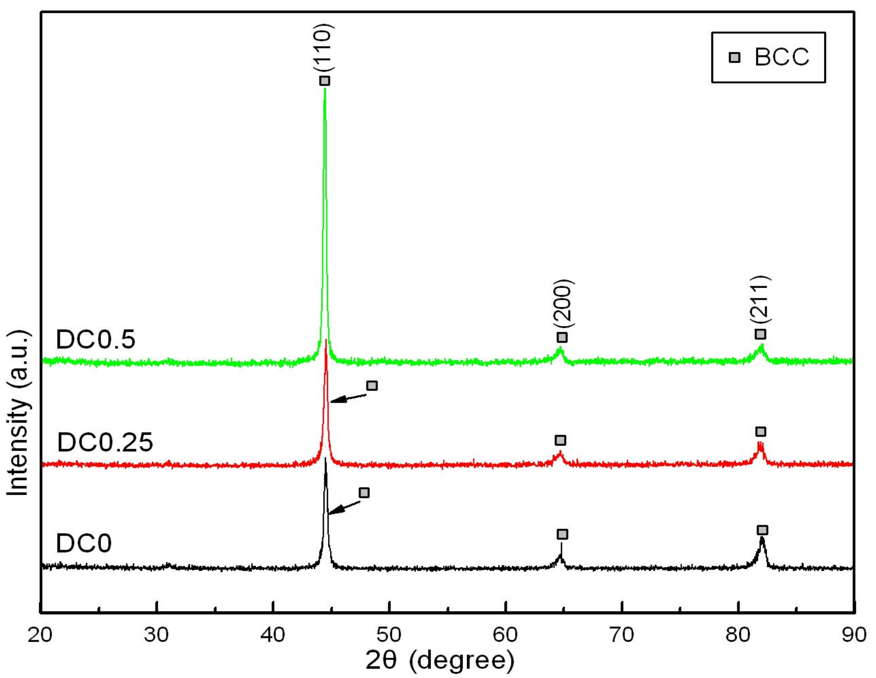


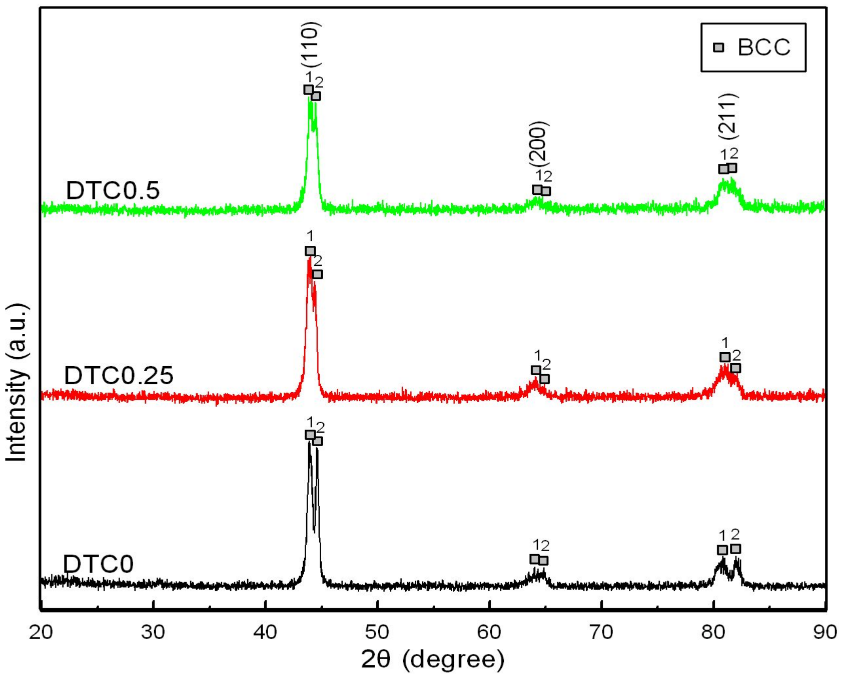
3.579A $CoCrFeNiCu_{1-y}Al_y$ $Ti_{0.5}CoCrFeNiCu_{1-y}Al_y$

FCC → BCC, High APE to Lower APE, with larger atoms Al

Cu=1.278A

(y=0, 0.25, 0.5)





$CoCrFeNiAlCu_y$ $Ti_{0.5}CoCrFeNiAlCu_y$

No PHASE TRANSITION

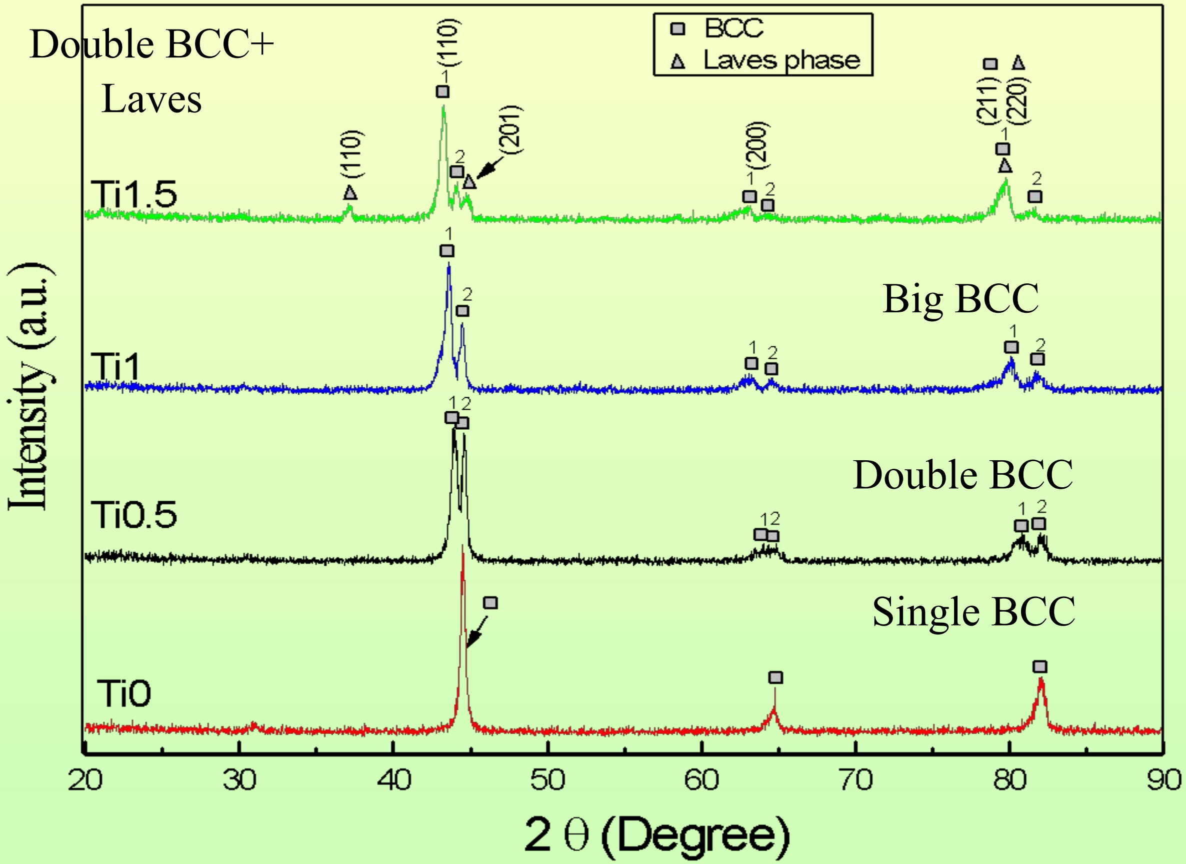
Co=1.251A

Biger BCC1phase:2.913A;
Smaller BCC2phase:2.872A

The smaller BCC transit to FCC firstly after adding Co

Ti=1.448A

$[Al_1Co_1Cr_1Fe_1Ni_1]Ti_x$ alloys



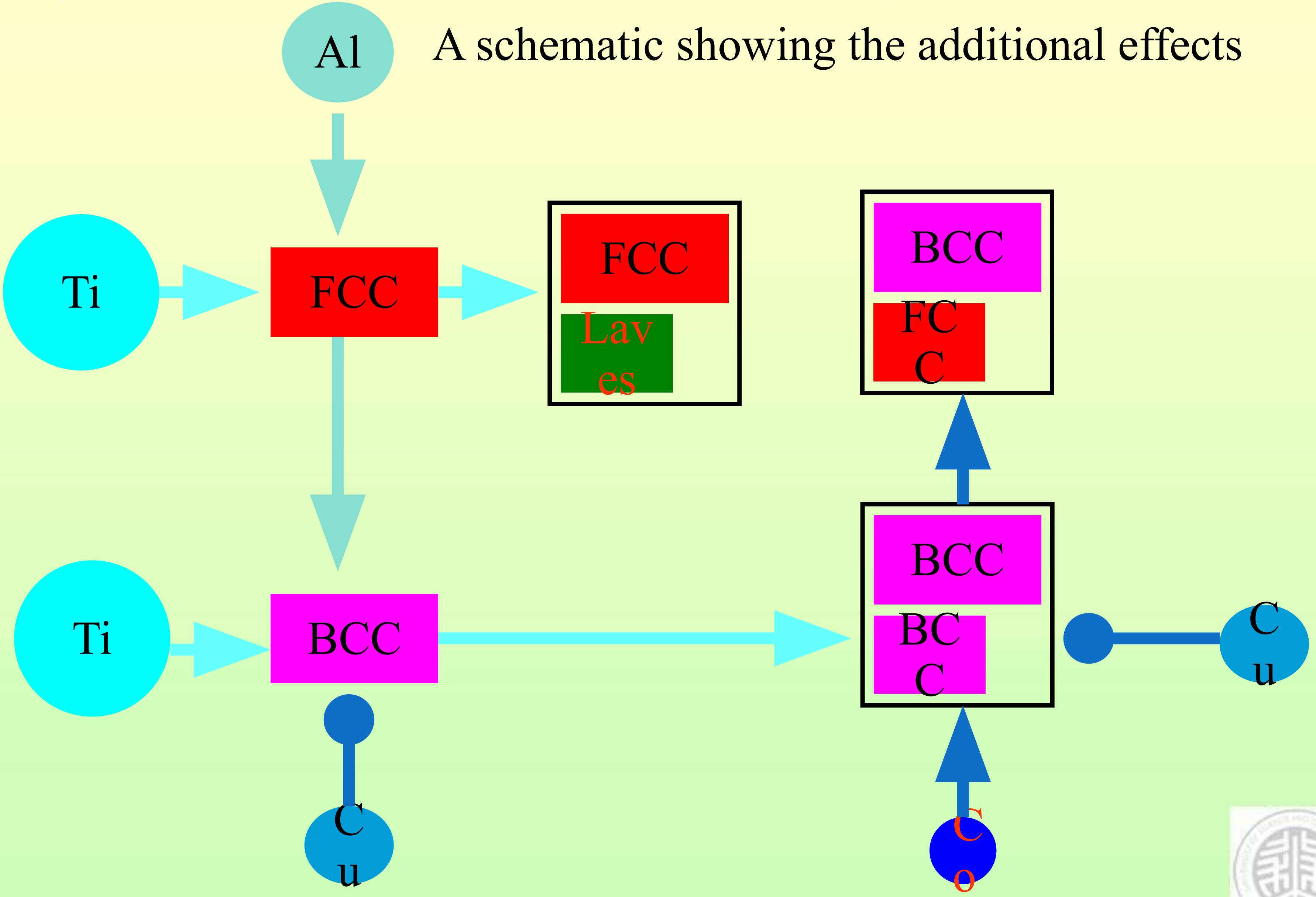
BCC+Ti ➔ BCC+BCC

After adding Ti, Laves phase forms

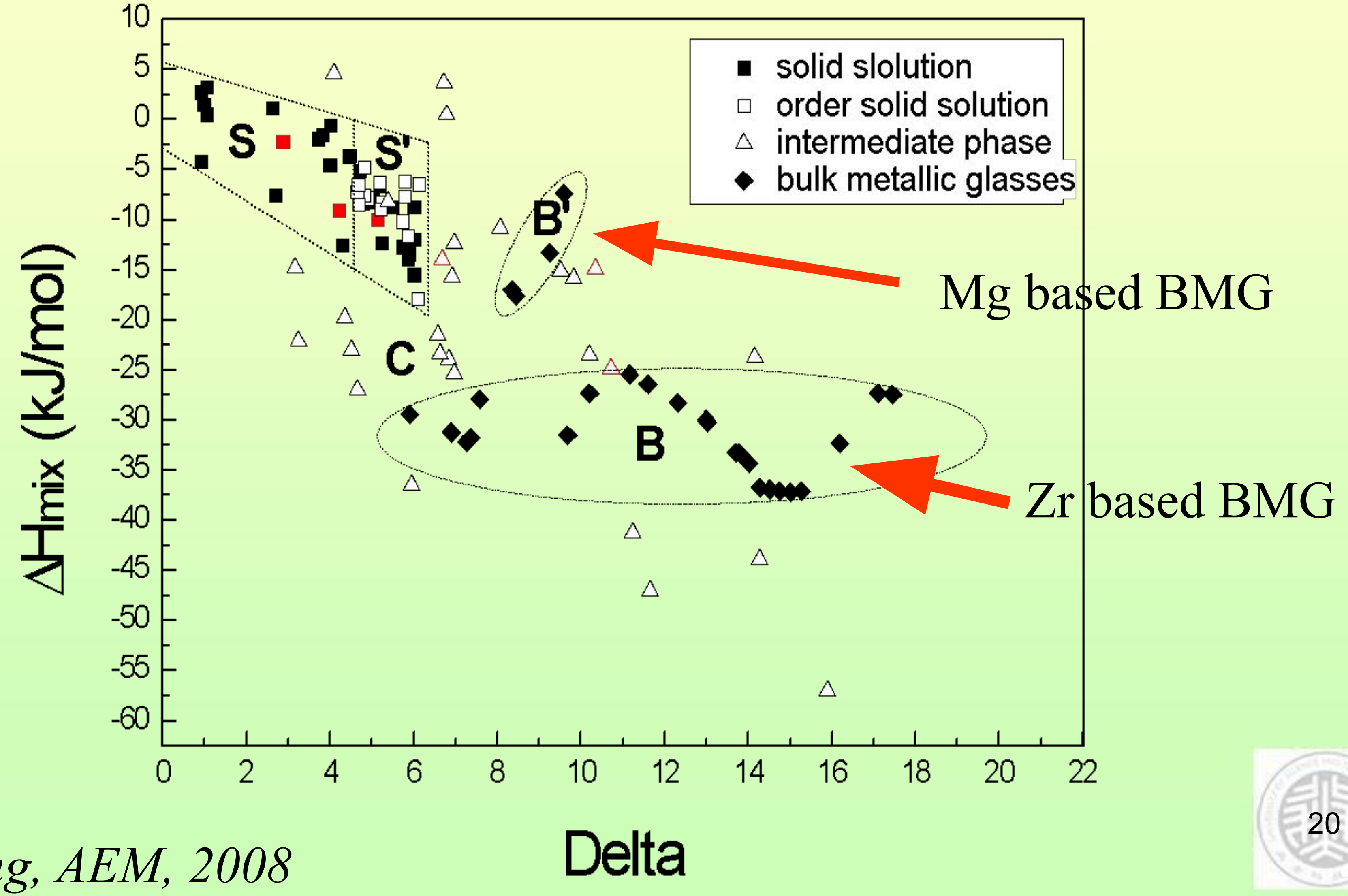
The transition is mainly lattice distortion induced and APE related

Zhou, APL, 2008

A schematic showing the additional effects



2.2. Considering of the enthalpy of mixing ΔH_{mix}



Zhang, AEM, 2008

2.3. Considering of the entropy of mixing ΔS_{mix}

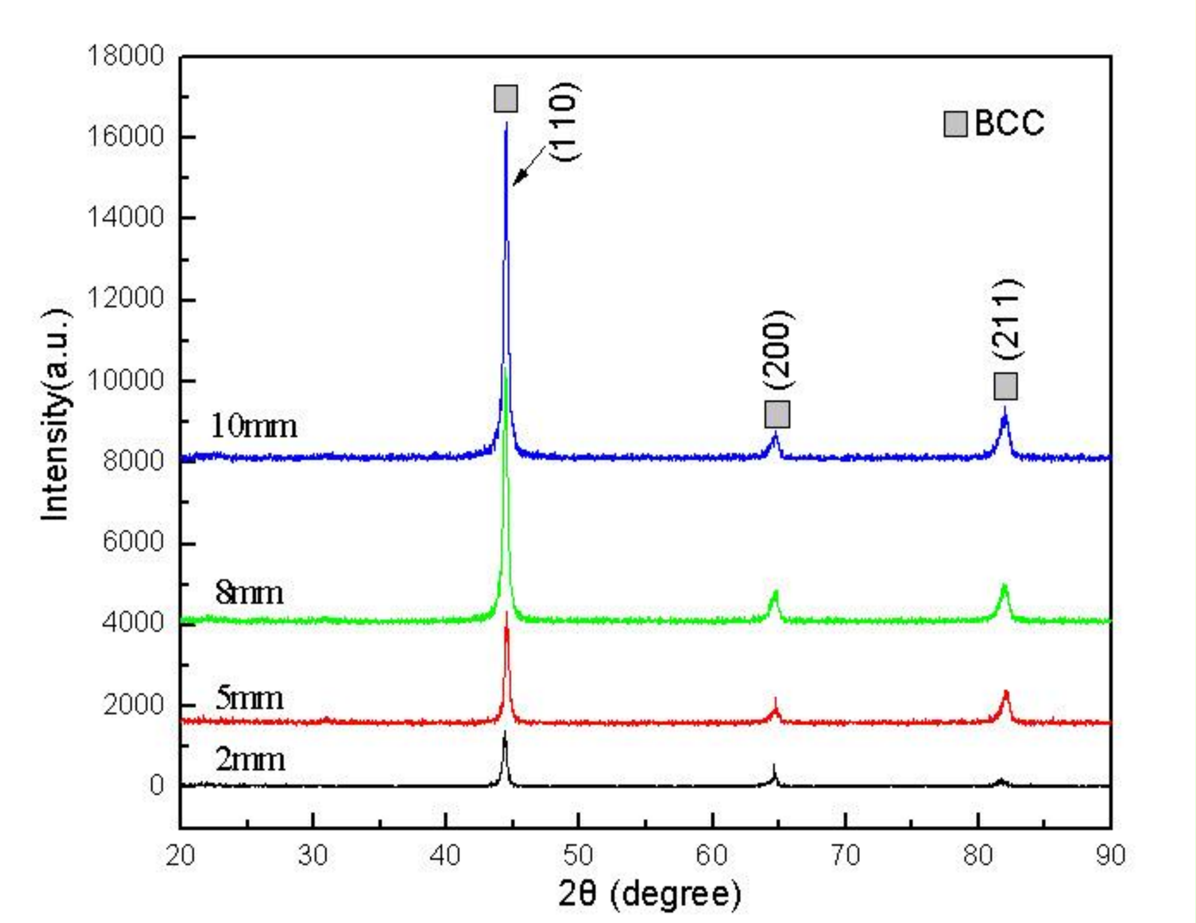
Adam－Gibbs 方程

$$\eta = \eta_0 \times \exp\left[\frac{C}{TS_c(T)}\right]$$

Here, C is a free enthalpy barrier to cooperative rearrangements. high entropy of mixing will lead to low viscosity, and a high mobility of the atoms in the liquid, thus a lower glass forming ability, this maybe the reason why the entropy of mixing for the bulk metallic glass forming alloys generally have a lower entropy of mixing , this maybe in some contradiction to the confusion principle.

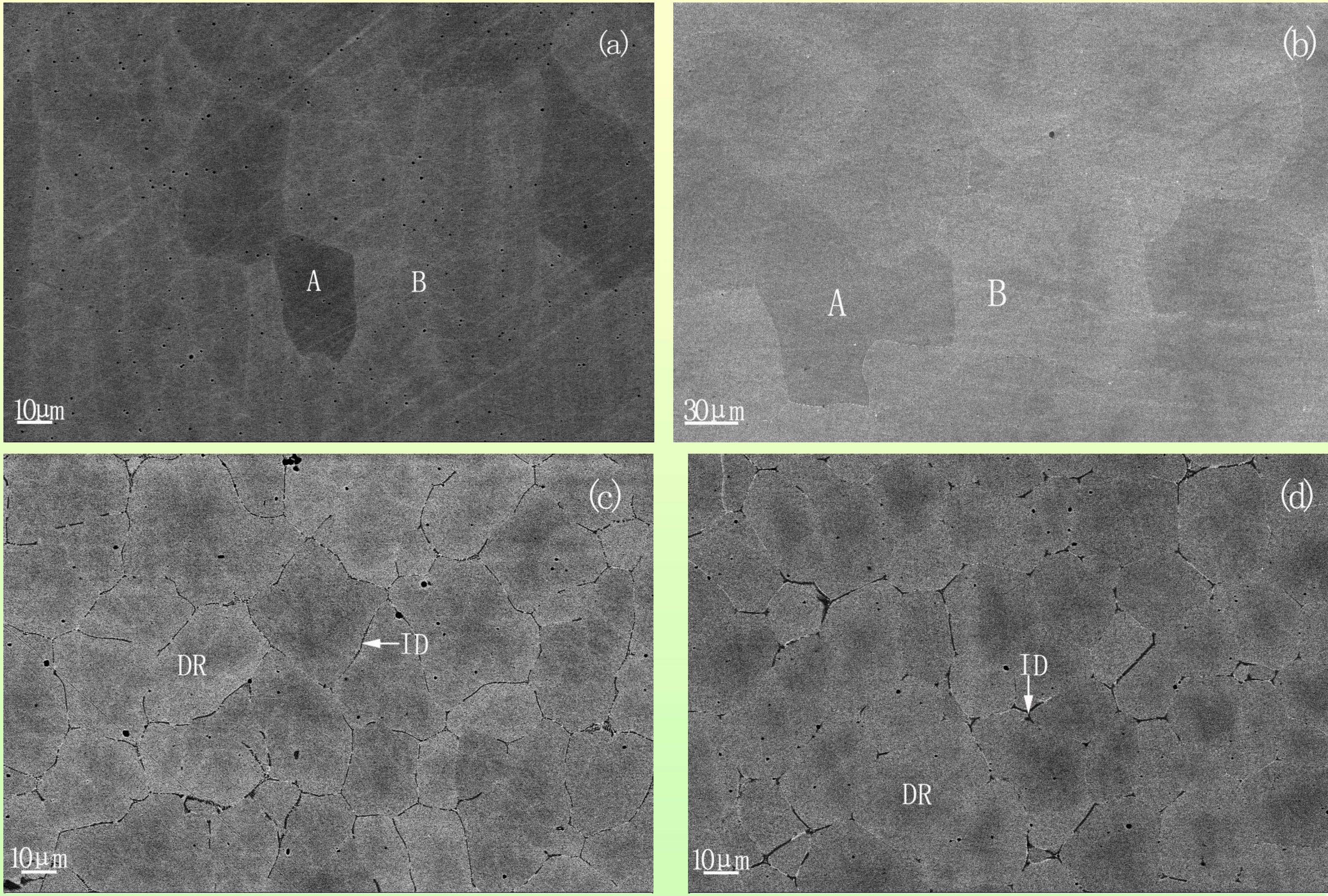
High Entropy is not good for the formation of BMG

2.4 Cooling Rate



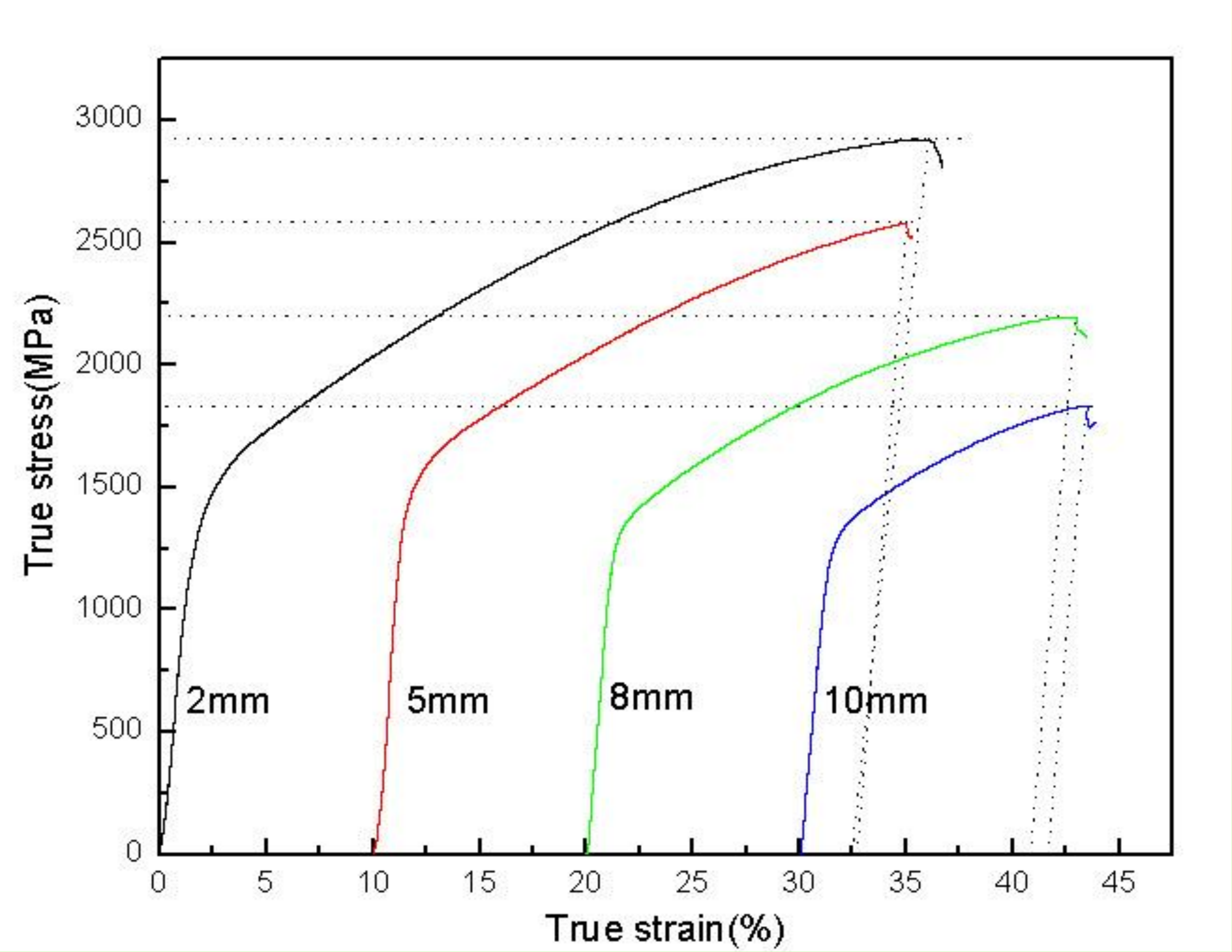
AlCoCrFeNi

2mm 5mm



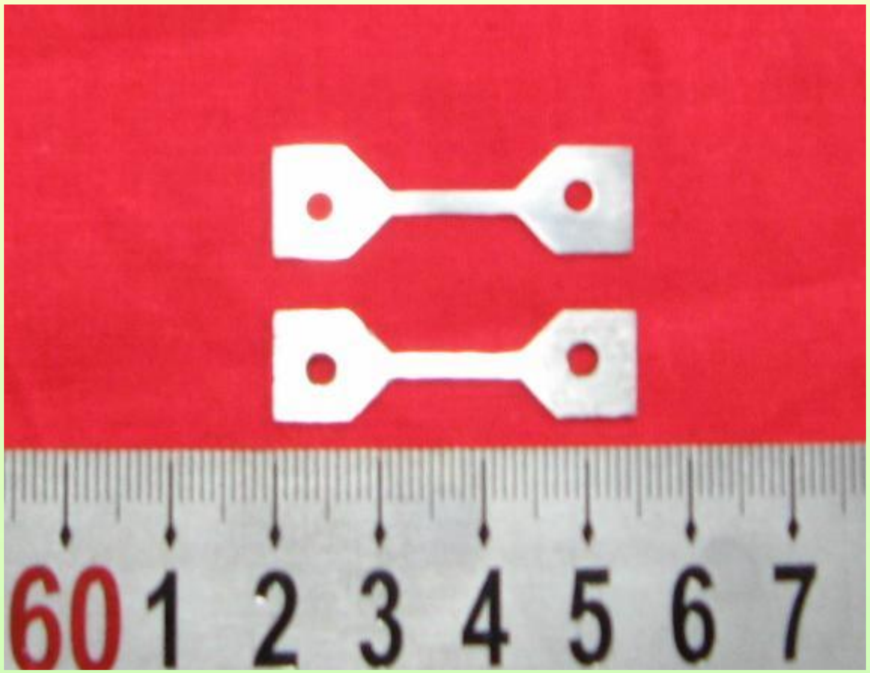
8mm 10mm

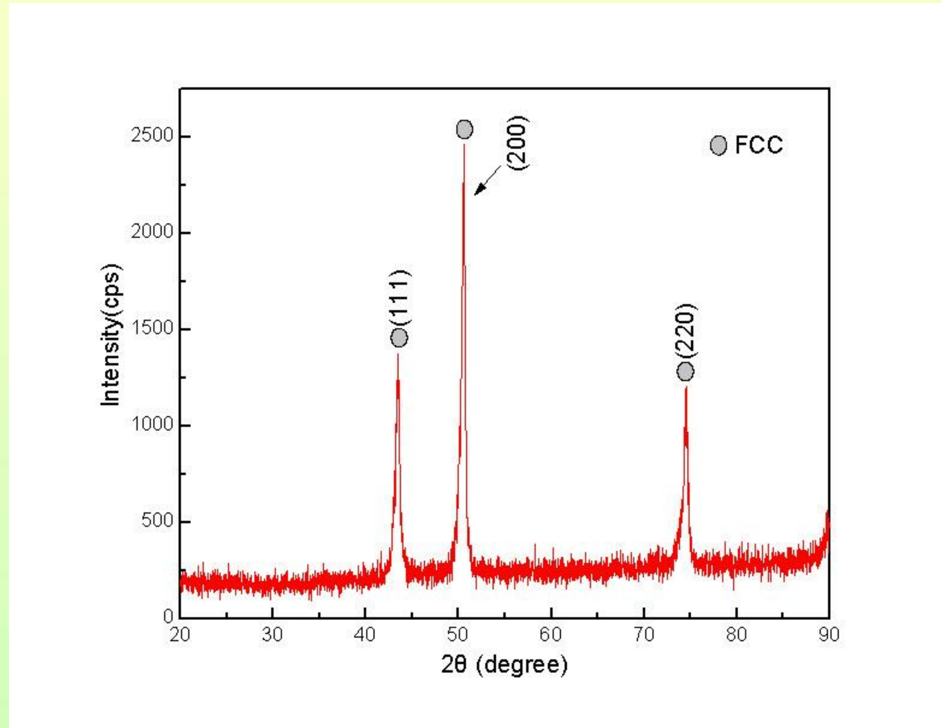
AlCoCrFeNi


3000
2500
2000
1500
1000
500
0
True stress(MPa)
0
5
10
15
20
25
30
35
40
45
True strain(%)
2mm
5mm
8mm
10mm

AlCoCrFeNi

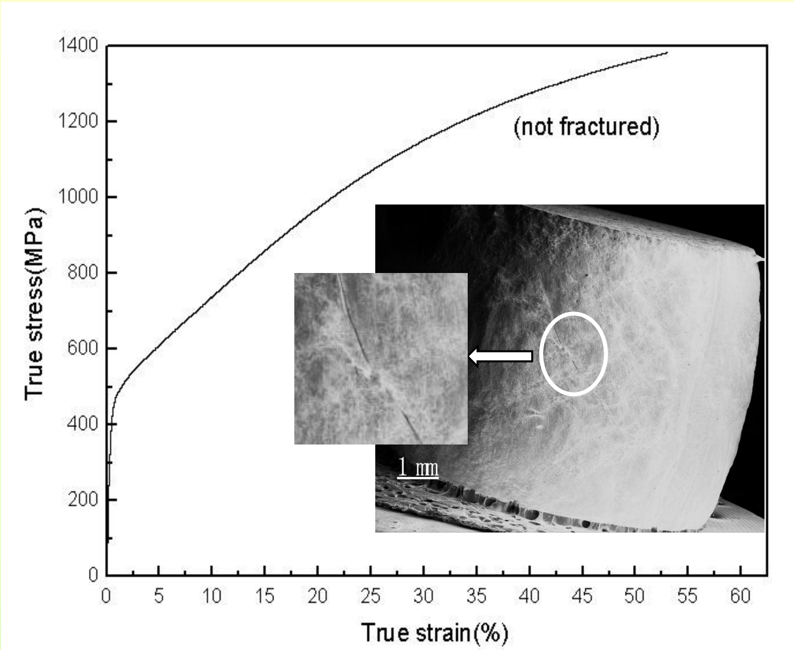
2.5 Tensile and Compressive properties





XRD pattern for the $CoCrCuFeNiAl_{0.5}$ alloy.

Φ5×10



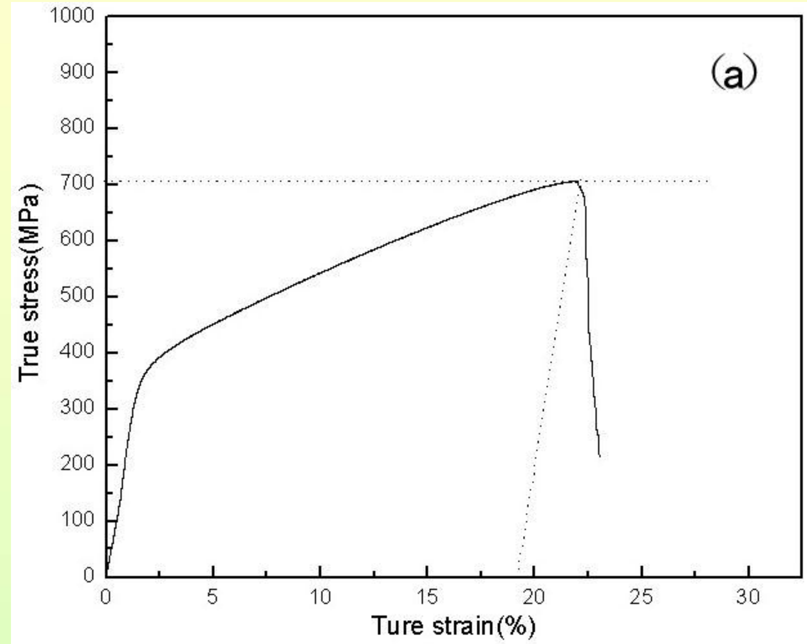


Table Room temperature mechanical test results for the CoCrCuFeNiAl0.5 alloy

This alloy	ε_P (%)	$\varepsilon_{0.2}$ (MPa)	σ_{max} (MPa)
Compressive	>51.5	460	>1380
Tensile	19.1	360	707

ε_P: plastic strain; $\varepsilon_{0.2}$: yield strength; σ_{max}: compressive/tensile strength

III. Summaries

1 Atomic size mismatch is the dominant factor for the phase formation of the high entropy alloys;

2 The formation of solid solution for the HEAs intends to have enthalpy of mixing close to zero;

3 High entropy of mixing facilitates the formation of the solid solution rather than the BMGs;

4 Cooling rate plays rather important role for the homogeneous microstructure than for the phase formation;

5 HEA can have tensile elongations as high as 19%.

Thanks for your attention