北京科技大学
University of Science and Technology Beijing

FeCoNiCrMn高熵合金的组织稳定性及变形行为

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北京科技大学　新金属材料国家重点实验室

Acknowledgements

- Students: W. H. Liu, S. Y. Li, H. L. Huang and Z. F. Lei
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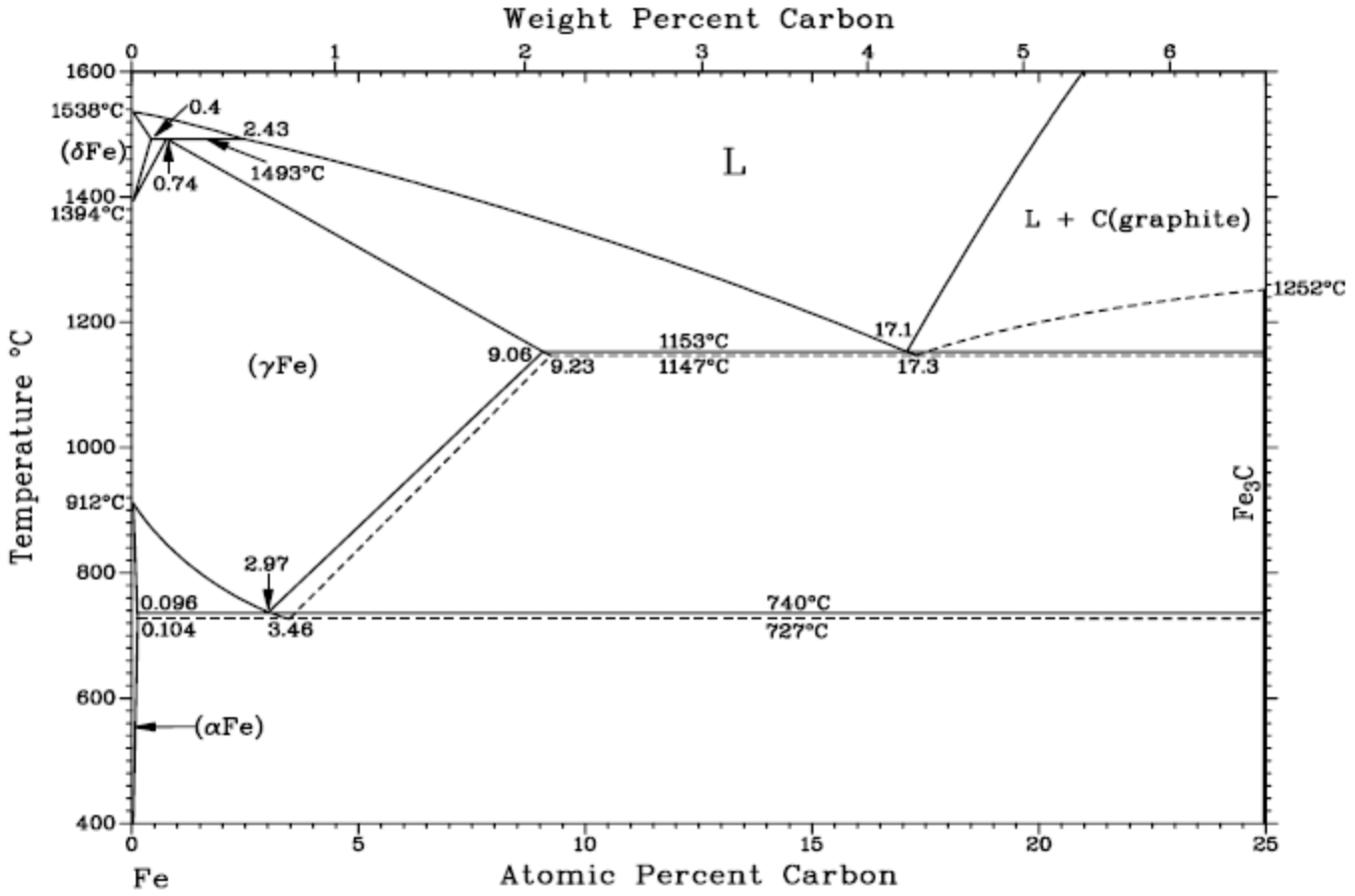
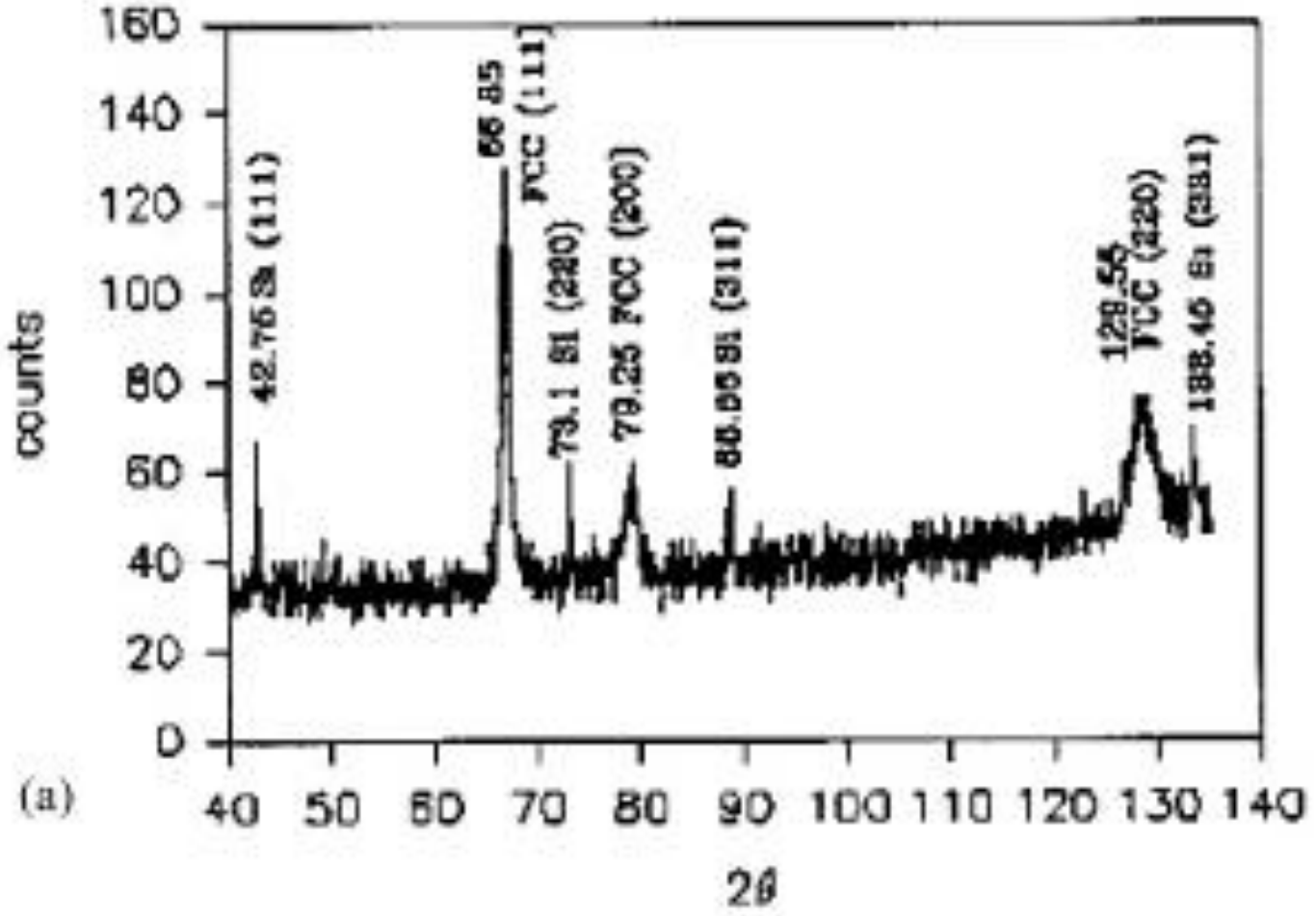
- “111” Program (B07003)
- Program for Innovative Research Team in University

Traditional alloys are mostly based on one primary element



Steels (Fe), Al alloys, Ti alloys, Mg alloys, Supper alloys (Ni)

Discovery of high entropy alloys



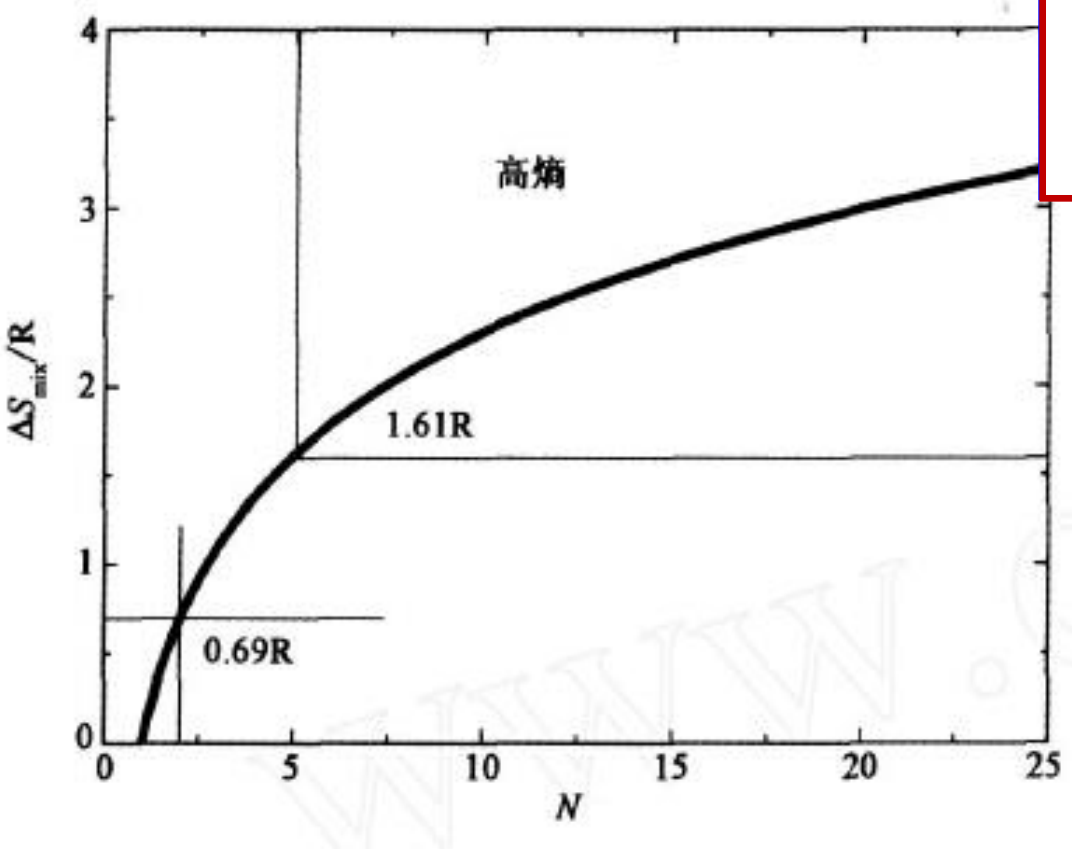
In 2004, Multicomponent FeCoNiCrMn alloy firstly reported by Cantor B. with a simple fcc solid-solution structure.

Cantor B et al. MSE A, 2004, 375-377: 213-218.

Definition of high entropy alloys

$$\Delta S_{mix} = R \ln N$$

$\ln c_i$



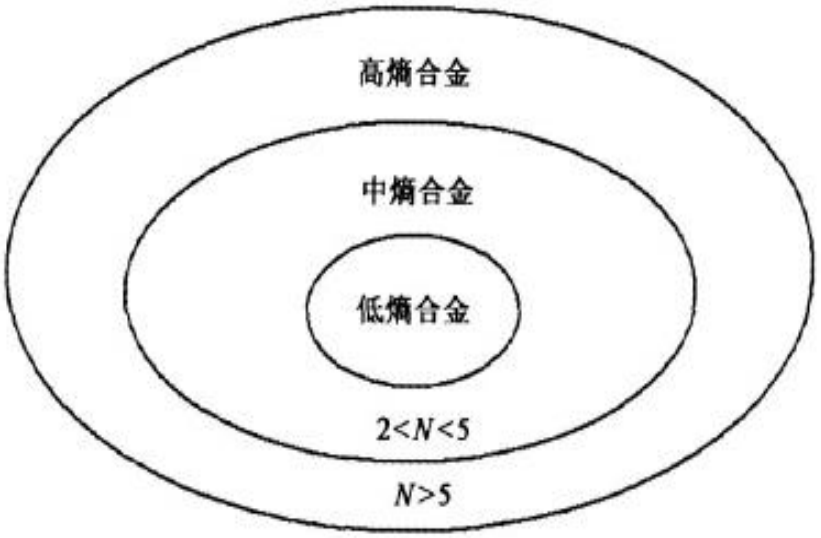


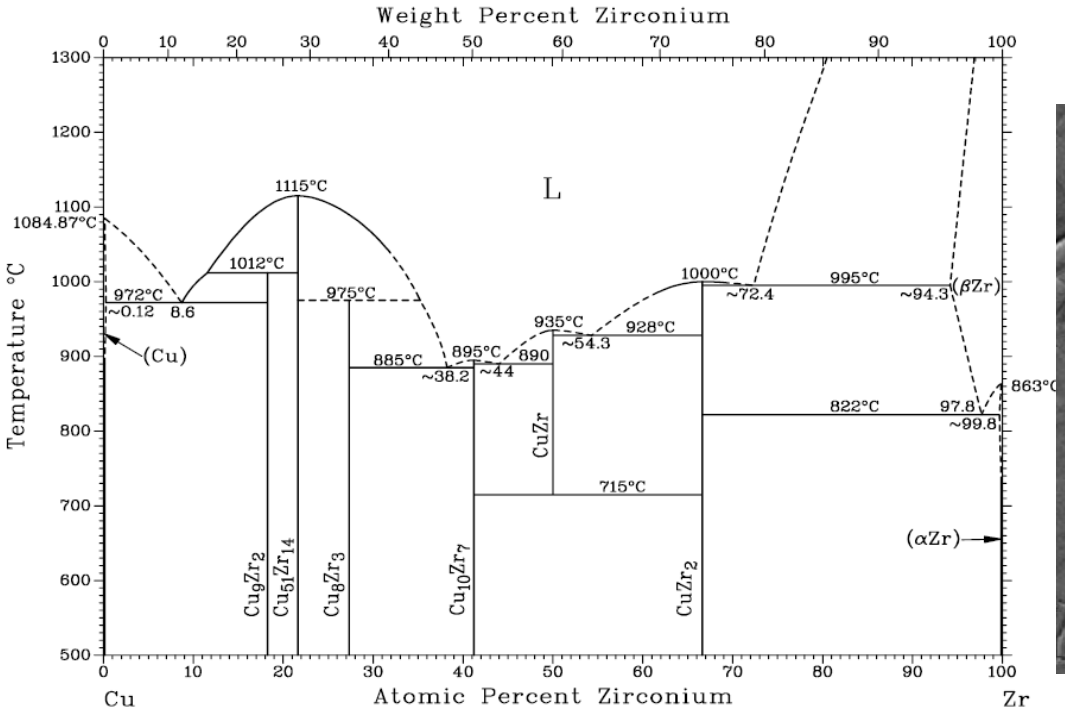
图 2 以混合熵划分的合金世界 [6]

Still in 2004, the concept of high entropy alloy was firstly introduced by Yeh JW

Yeh JW et al. Adv Eng Mater, 2004, 6: 299-303.

Simple phase formation but complex metallurgical phenomenon

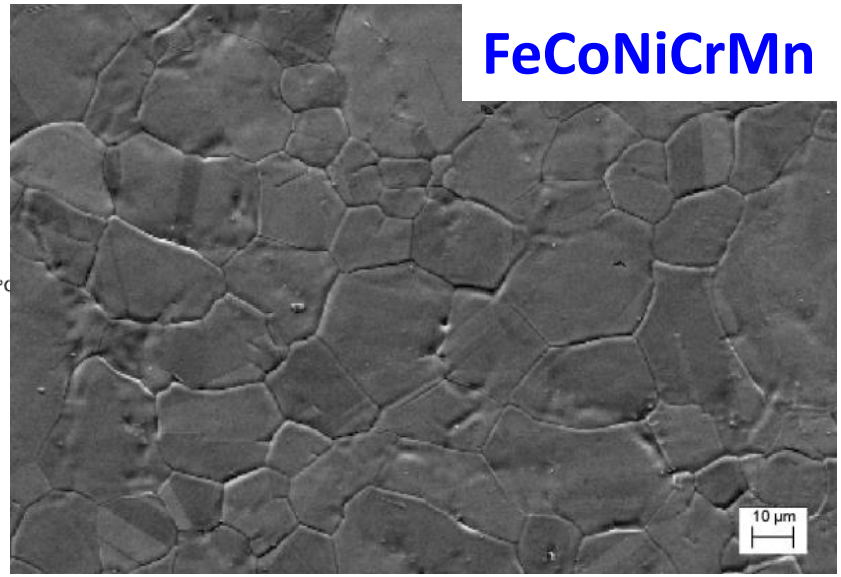
Cu-Zr binary alloy system



The Gibbs Phase Rule

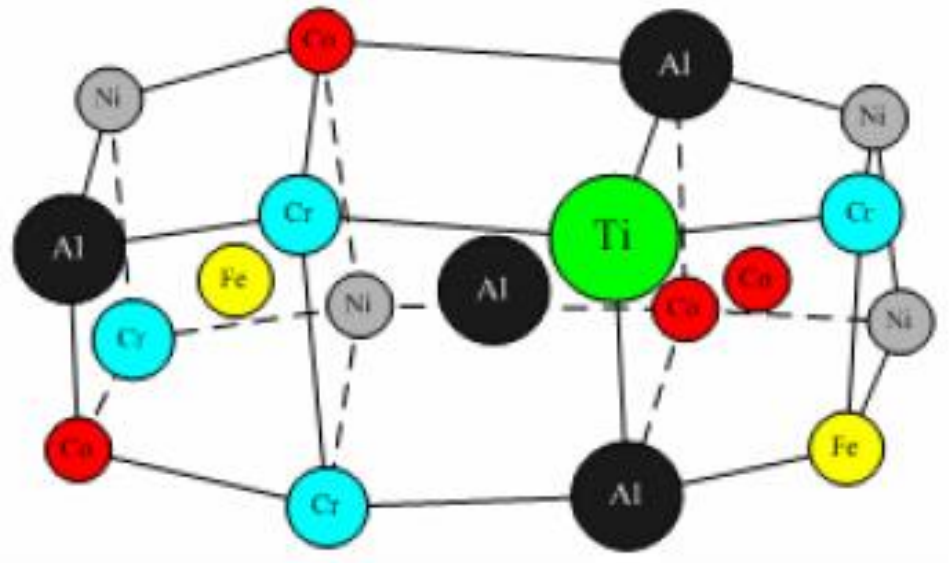
P=N+1-F

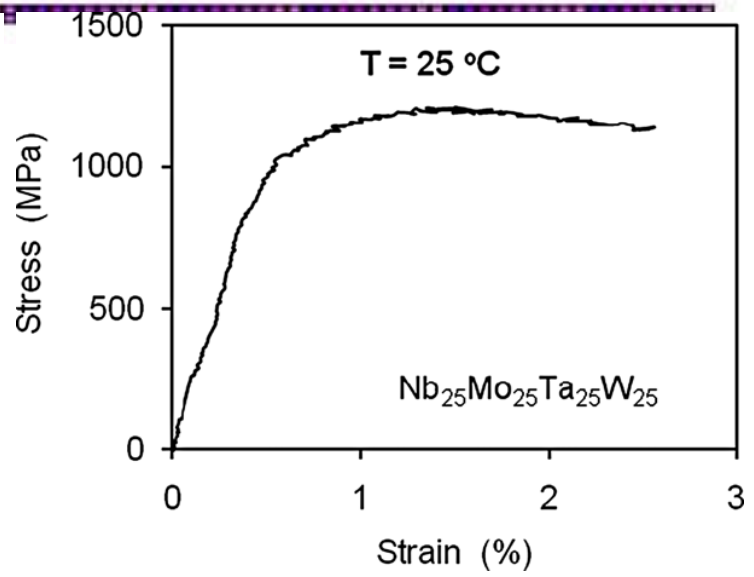
When N=5, P=6



Actually HEAs alloy have a simple solid-solution structure (mainly fcc or bcc) !!

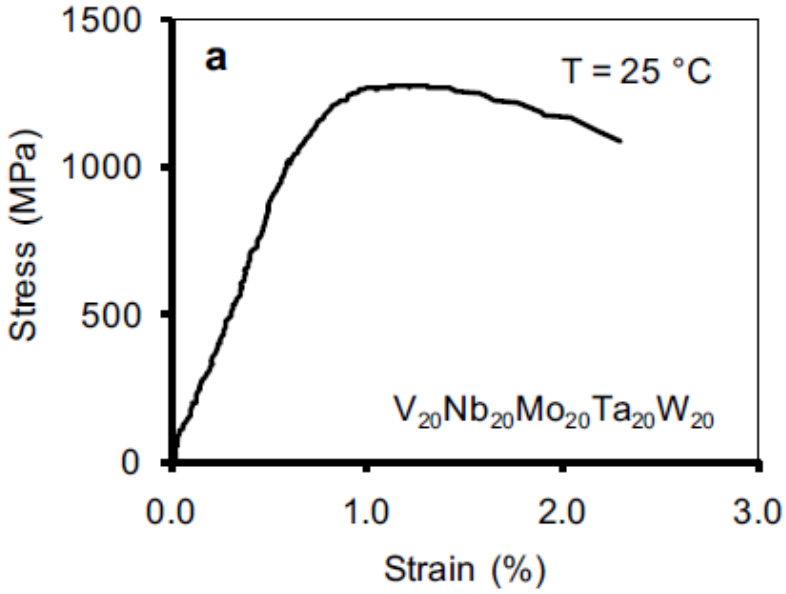
Features of HEAs——severe lattice distortion





Lattice distortion

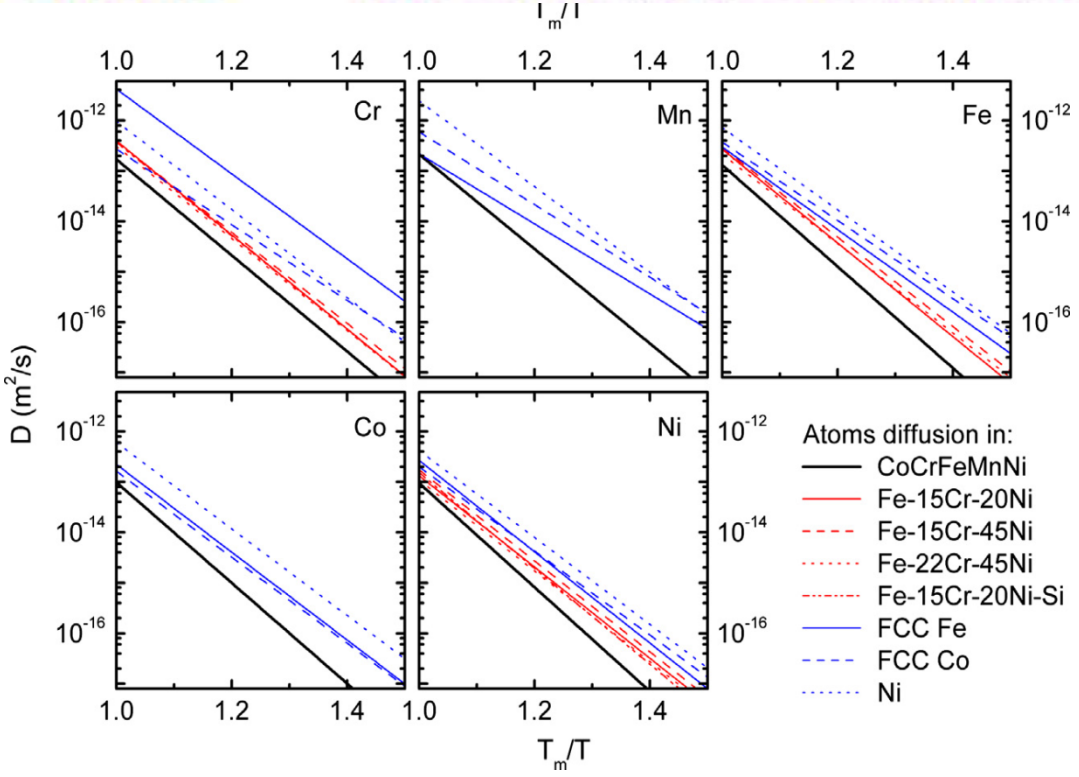
Solution strengthening effect

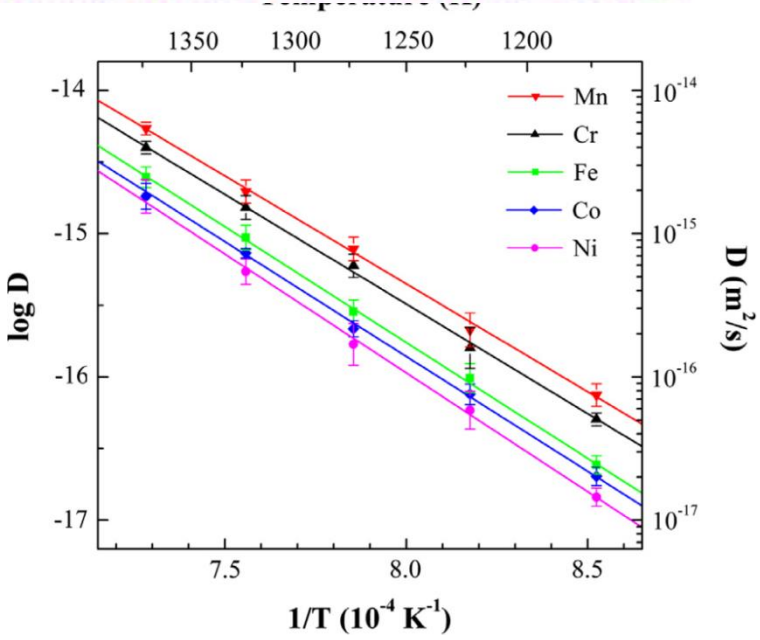


Zhou, et al. Appl Phys Lett, 2008, 92: 241917

Senkov ON, et al. Intermetallics, 2011,19:698

Features of HEAs——sluggish diffusion

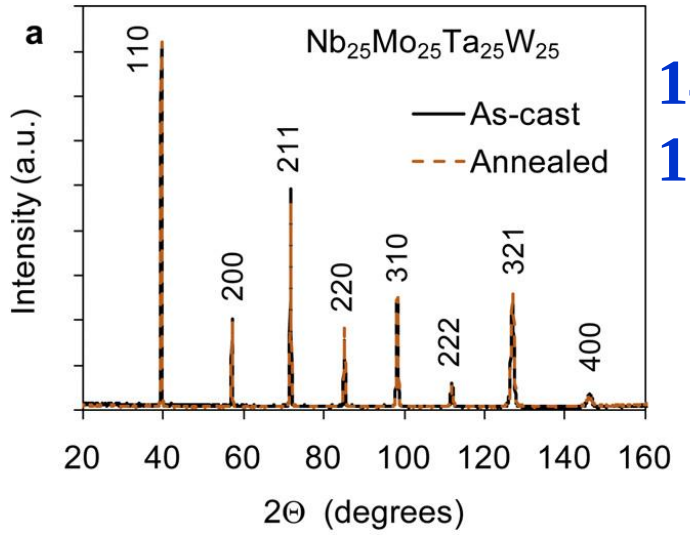


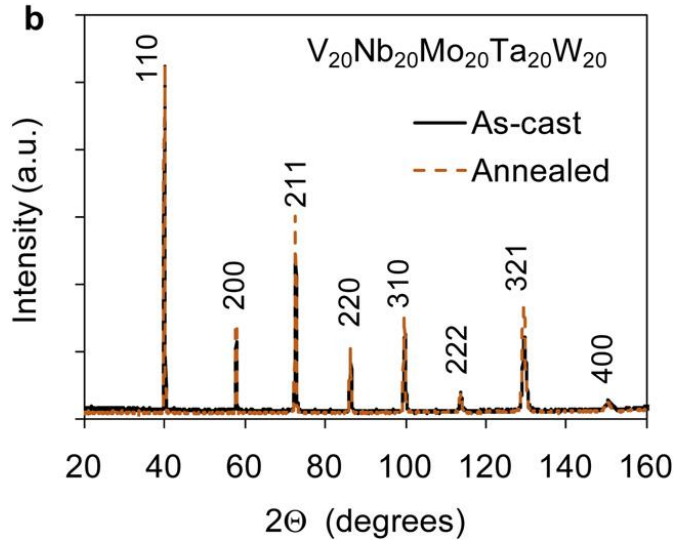


- Constituent elements in the HEA matrix diffuse much slowly over the entire temperature range
- The diffusion coefficient of Ni is the smallest among that of all constituents

Tsai et al. Acta Mater 2013; 61:4887

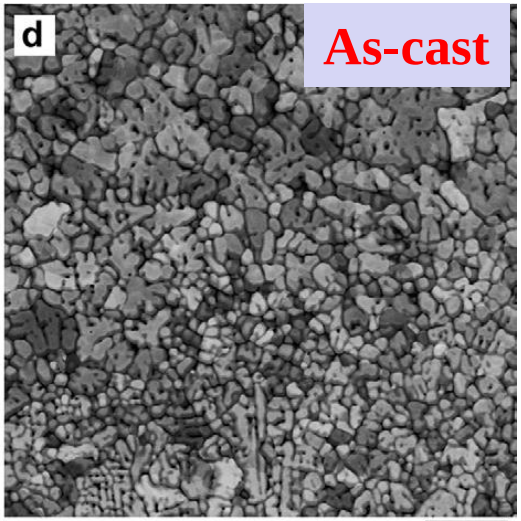
Features of HEAs——high phase stability

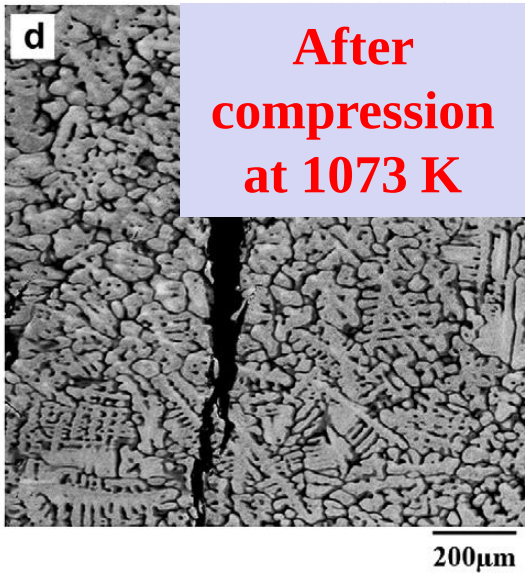




1400°C
19h

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

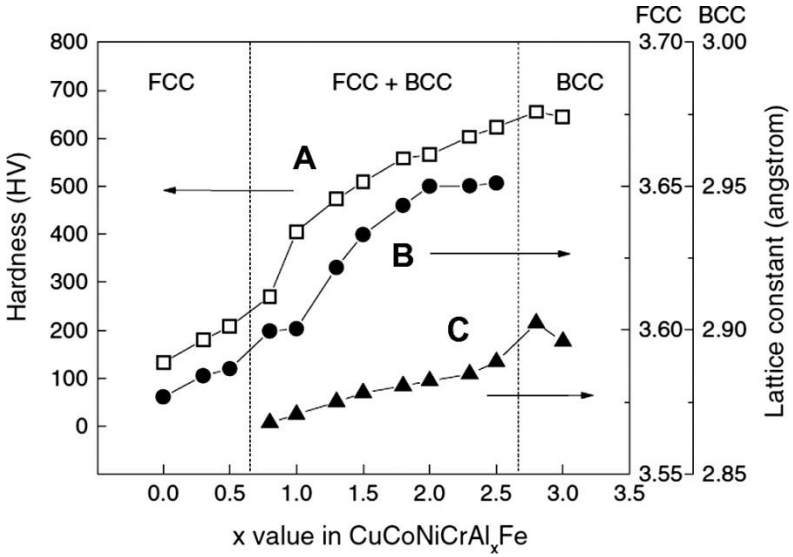




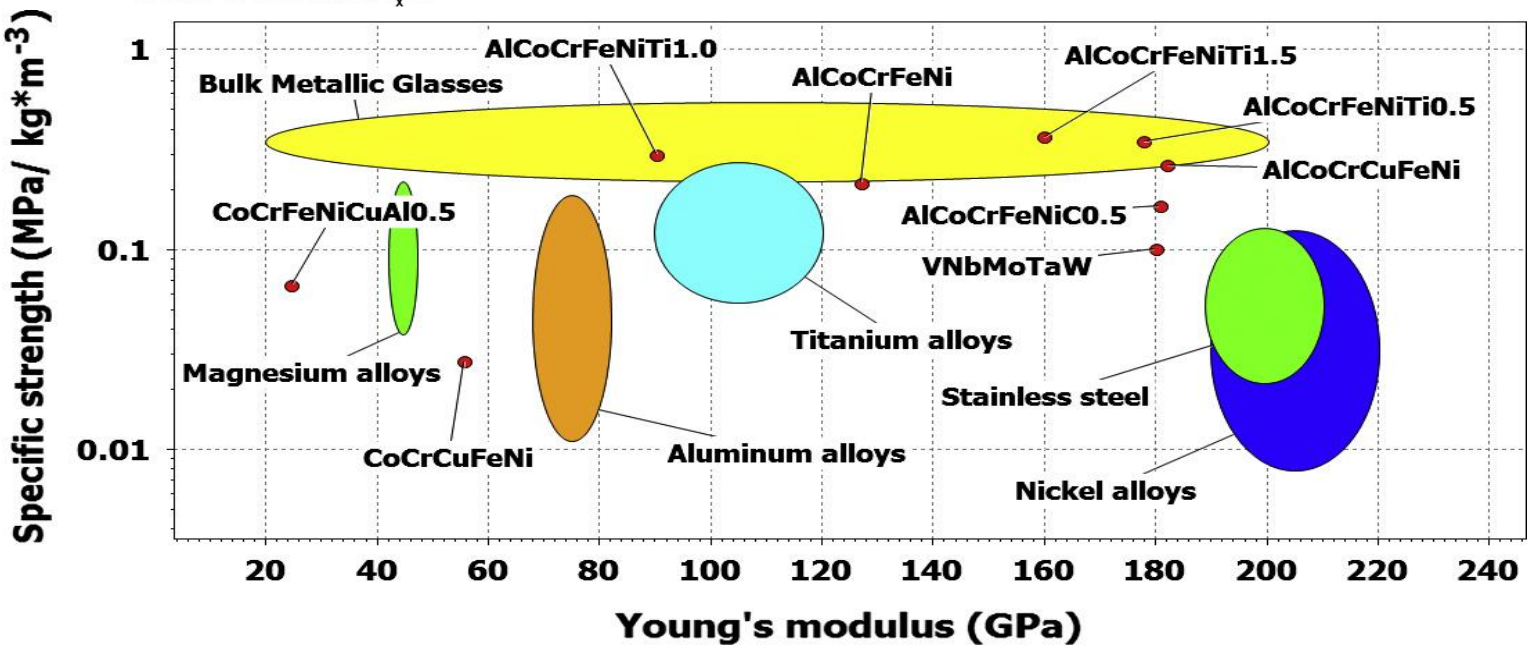
- Formation of a single *bcc* phase
- The *bcc* phase is highly stable up to 1600 °C

Senkov et al. Intermetallics 2011; 19: 698-706

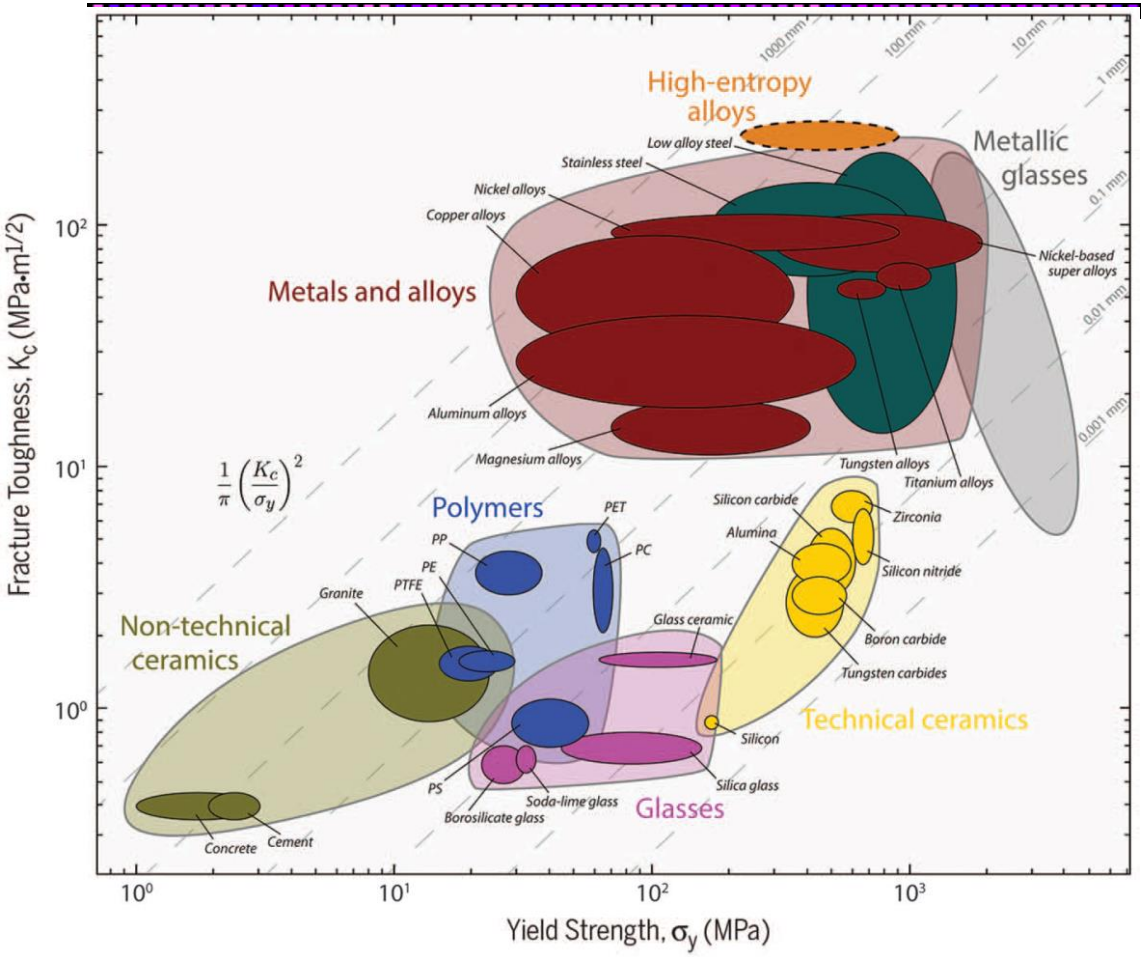
Features of HEAs——cock tail effect



➢the effect indicates that the unexpected properties can be obtained after mixing many elements, which could not be obtained from any one independent element.



Extremely high toughness of a typical fcc HEA

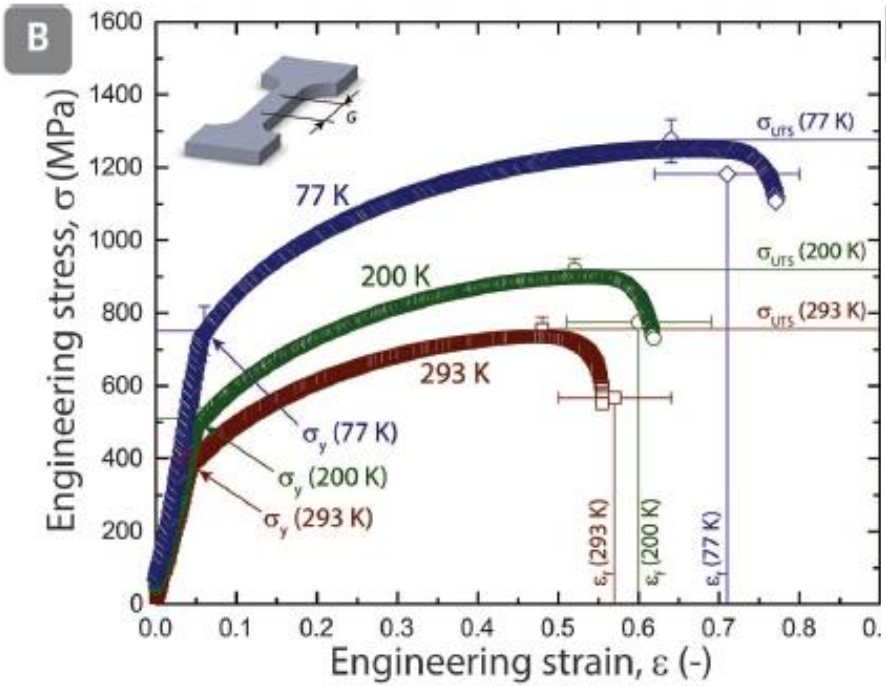


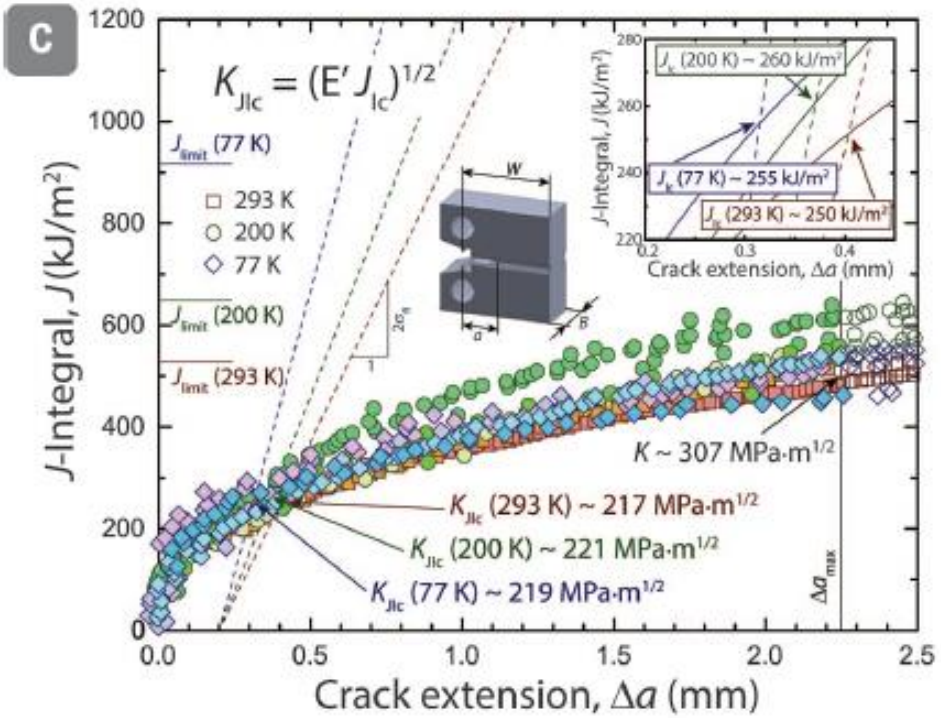
Science
AAAS

➢ **The fracture toughness of FeCoNiCrMn exceeds 210 MPa m$^{-1/2}$**

Bernd Gludovatz et al.
Science 2014,345:1153

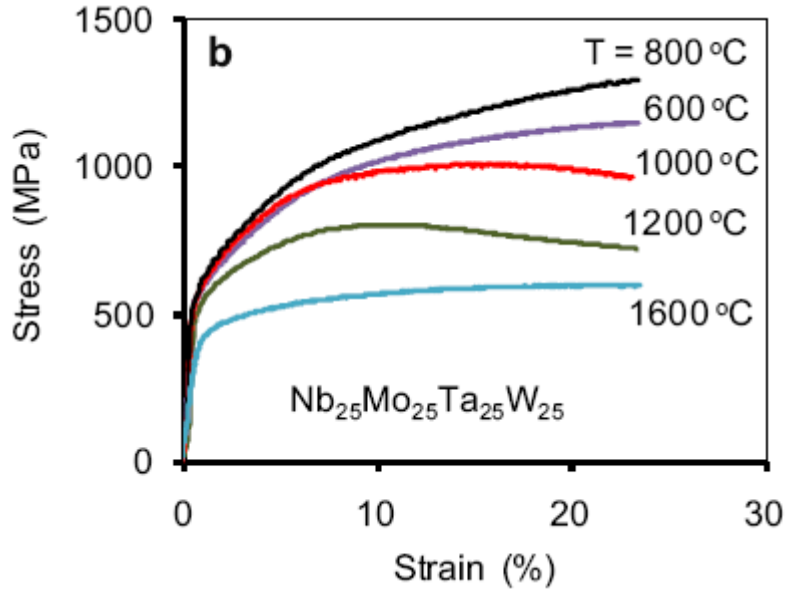
Abnormal low-temperature mechanical properties

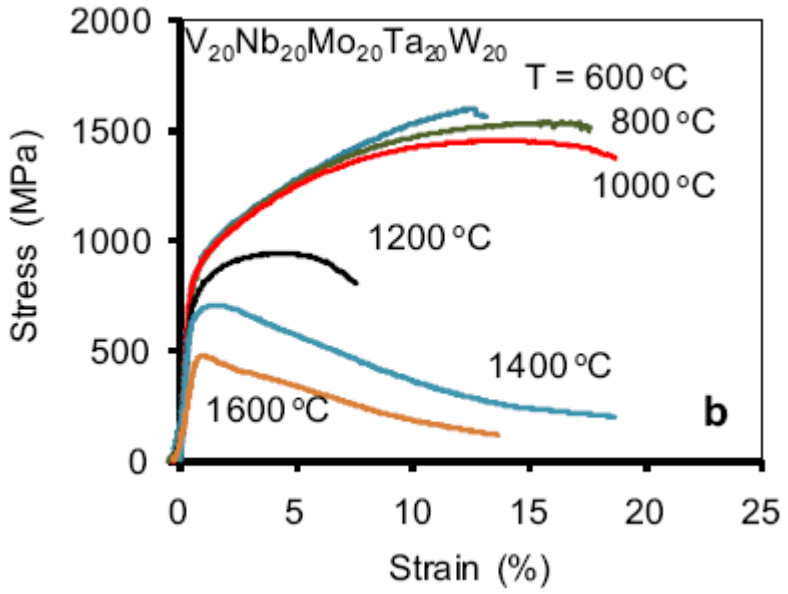




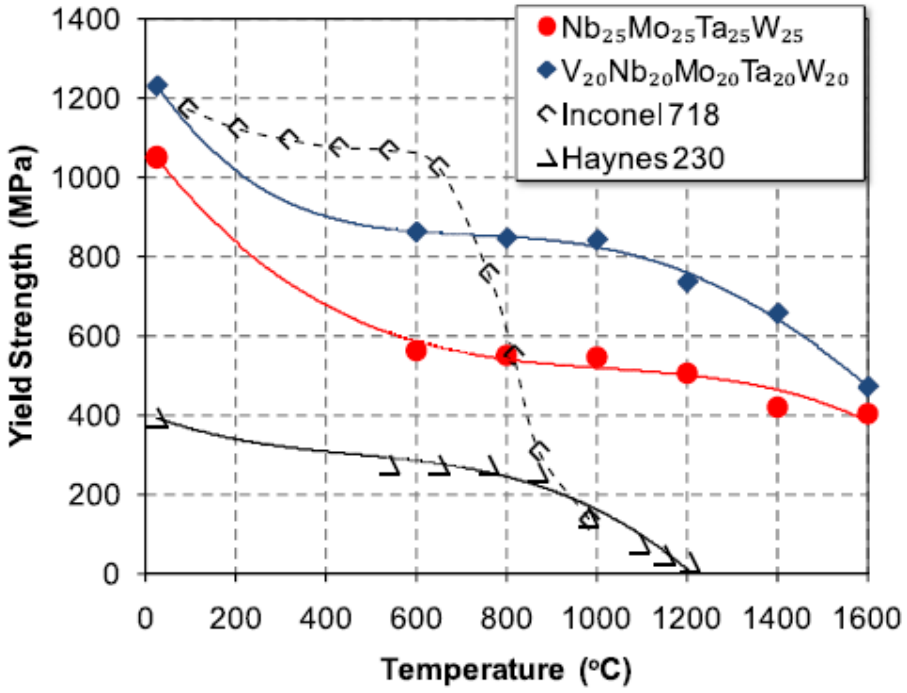
- With the decrease of testing temperature, both tensile strength and ductility are increased;
- The fracture toughness kept almost unchanged;

Promising high-temperature mechanical properties of bcc HEAs





Senkov et al. Intermetallics 2011; 19: 698-706



- **High yield strength at temperatures up to 1600°C**
- **The strong resistance to high-temperature softening, as compared to the superalloys**

Interesting physical properties of HEAs: discovery of superconductivity

PHYSICAL REVIEW LETTERS

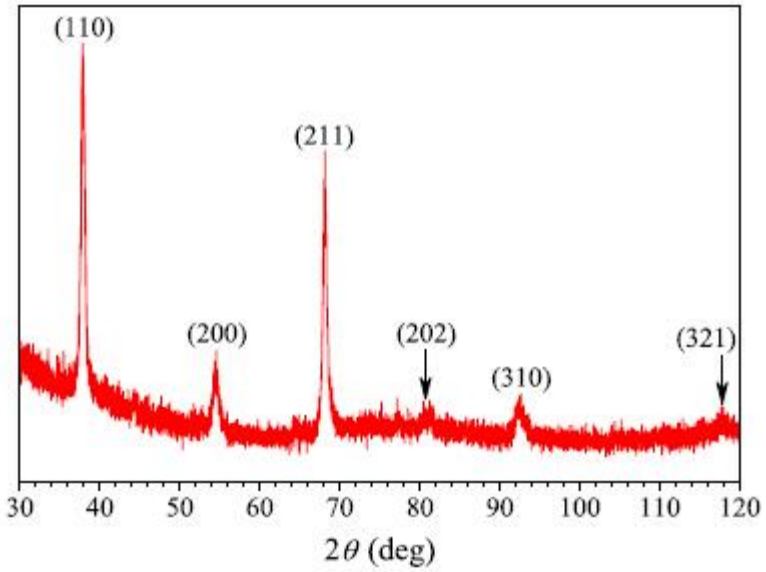


FIG. 1 (color online). X-ray diffraction pattern of the $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ HEA. The peaks are indexed to a bcc crystal lattice.

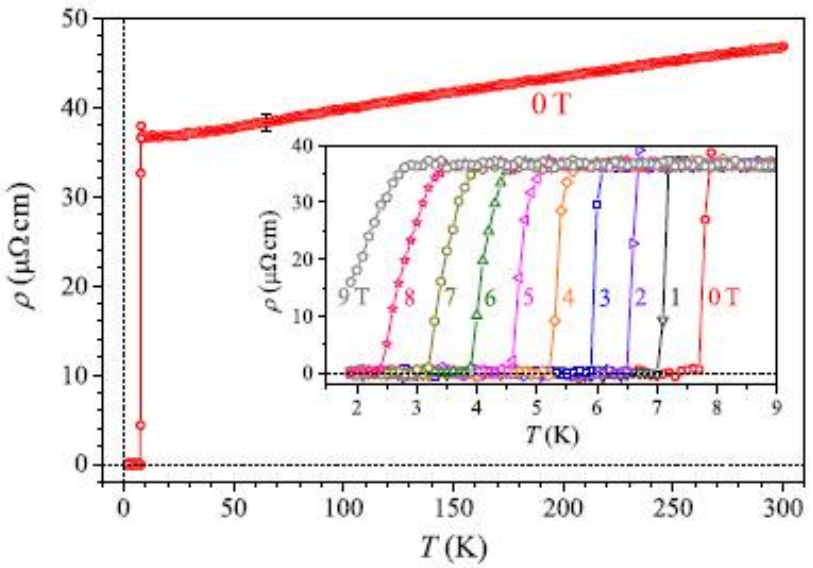


FIG. 2 (color online). Electrical resistivity in zero magnetic field between 300 and 2 K. Magnetic-field dependence of the resistivity in the region of the SC transition for fields up to 9 T is shown in the inset.

- $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ HEA possesses an body-centered cubic structure of lattice parameter a ≈ 3.36 Å.
- It is a type II superconductor with a transition temperature Tc ≈ 7.3 K

P. Koželj et al. PRL 2014,113: 107001

Diffusion barrier materials

G154

Journal of The Electrochemical Society, **157** (6) G154-G159 (2010)
0013-4651/2010/157(6)/G154/6/$28.00 © The Electrochemical Society

Ultrathin $(AlCrTaTiZr)N_x$/AlCrTaTiZr Bilayer Structures with High Diffusion Resistance for Cu Interconnects

Shou-Yi Chang[*,z] **and Dao-Sheng Chen**[**]

Department of Materials Science and Engineering, National Chung Hsing University, Taichung 40227, Taiwan

In this study, $(AlCrTaTiZr)N_{0.7}$ and $(AlCrTaTiZr)N_1$ films with quinary metallic elements were developed as diffusion b materials for Cu interconnects. To improve the interface adhesion to Cu, an AlCrTaTiZr buffer layer was deposited on the ba to form $(AlCrTaTiZr)N_{0.7}$/AlCrTaTiZr and $(AlCrTaTiZr)N_1$/AlCrTaTiZr bilayer structures. The as-deposited AlCrTaTiZ $(AlCrTaTiZr)N_{0.7}$ films were amorphous structures, and $(AlCrTaTiZr)N_1$ possessed a nanocomposite structure. After anneal 800°C, although Cu penetrated into the AlCrTaTiZr buffer layer, the diffusion of Cu was retarded by the $(AlCrTaTiZr)N_0$ $(AlCrTaTiZr)N_1$ barriers. During annealing at 900°C, the interdiffusion of Si and Cu occurred through $(AlCrTaTiZr)N_{0.7}$/AlCrTaTiZr bilayer, and Cu silicides formed. However, the $(AlCrTaTiZr)N_1$/AlCrTaTiZr bilayer remained stable. Neither the interdiffusion of Cu and Si through the $(AlCrTaTiZr)N_1$/AlCrTaTiZr bilayer nor the silicide formation was identified, indicating the high diffusion resistance of the bilayer structure.
 [DOI: 10.1149/1.3374194]

Manuscript submitted July 6, 2009; revised manuscript received February 16, 2010. Published May 3, 2010. This was Paper 10 presented at the Vancouver, Canada, Meeting of the Society, April 25–30, 2010.

- **High phase stability ----no interaction with substrates;**
- **Low diffusion kinetics-- --high diffusion resistance at elevated temperatures**

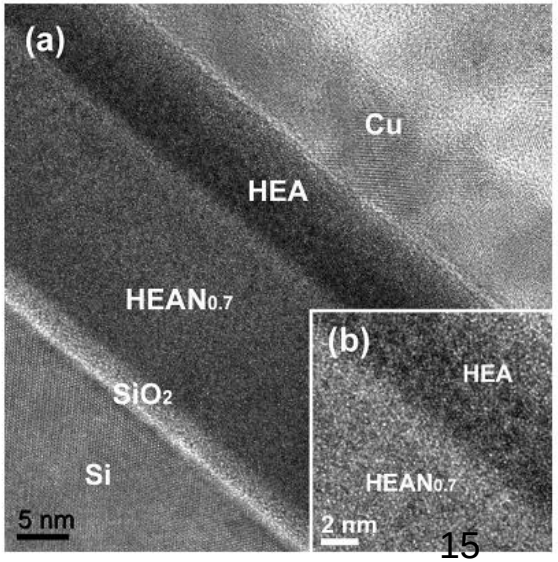


Figure 2. (a) HRTEM image of as-deposited Si/$HEAN_{0.7}$/HEA/Cu film stack and (b) lattice image in $HEAN_{0.7}$/HEA region at a high magnification.

The research activities on HEAs at USTB

APPLIED PHYSICS LETTERS **90**, 181904 (2007)

Solid solution alloys of $AlCoCrFeNiTi_x$ with excellent room-temperature mechanical properties

Y. J. Zhou, Y. Zhang,[a)] Y. L. Wang, and G. L. Chen
State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Bei, Beijing 100083, China

(Received 9 February 2007; accepted 3 April 2007; published online 30 April 2007)

Alloys with composition of $AlCoCrFeNiTi_x$ (x: molar ratio; x=0, 0.5, 1, 1.5) were designed b the strategy of equiatomic ratio and high entropy of mixing. The alloy system is composed of body centered cubic solid solution and possesses excellent room-temperature comp mechanical properties. Particularly for $AlCoCrFeNiTi_{0.5}$ alloy, the yield stress, fracture streng plastic strain are as high as 2.26 GPa, 3.14 GPa, and 23.3%, respectively, which are superior of the high-strength alloys such as bulk metallic glasses. © *2007 American Institute of P*
[DOI: 10.1063/1.2734517]

Progress in Materials Science 61 (2014) 1–93

Microstructures and properties of high-entropy alloys

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[c] *National Energy Technology Laboratory, 1450 Queen Ave SW, Albany, OR 97321, USA*
[d] *URS Corporation, PO Box 1959, Albany, OR 97321-2198, USA*
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Progress in Materials Science, 2014; 61:1-93

Our purpose

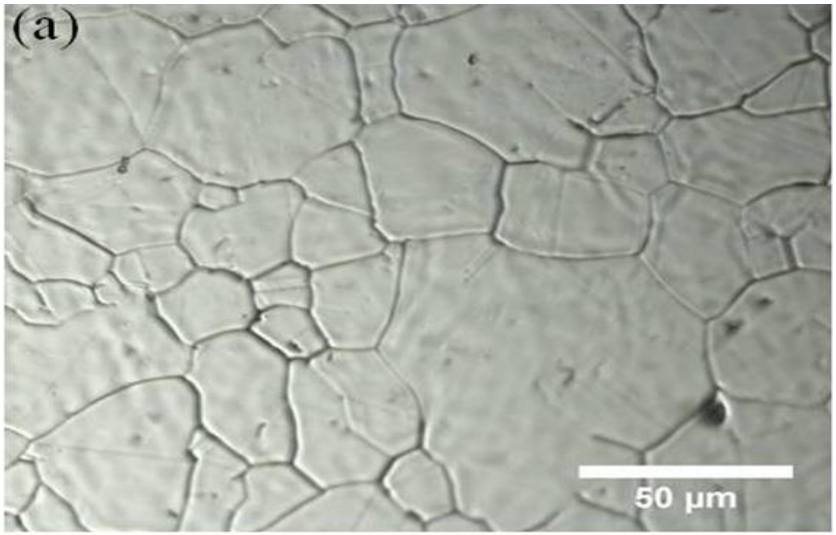
Design the FeCoNiCrMn based HEAs for high-temperature applications

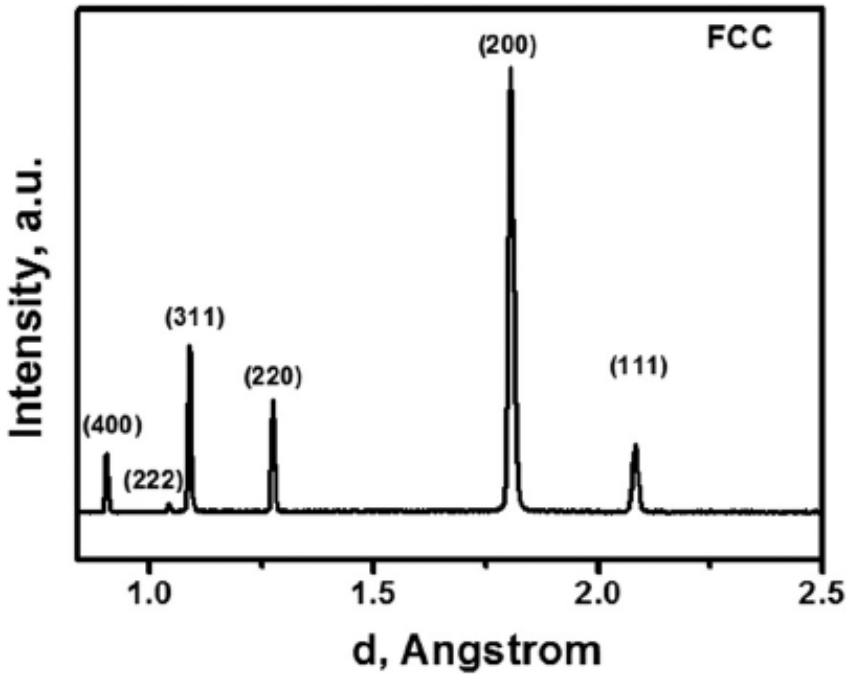
Content

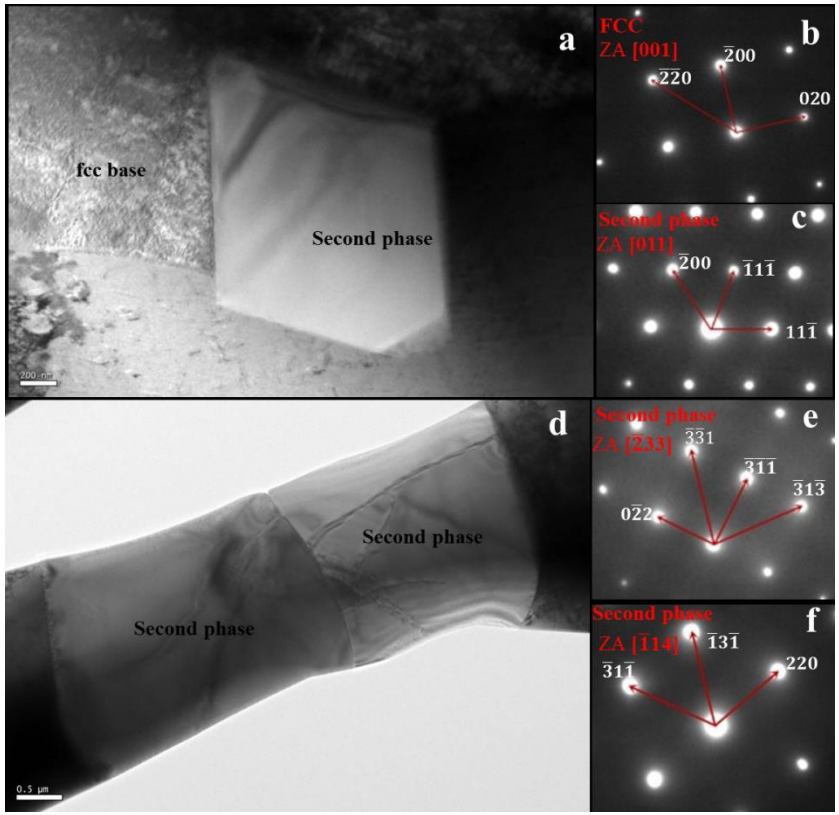
- Phase formation and stability
- Grain growth at elevated temperatures
- Deformation behavior
- Alloying effects (to enhance high-T mechanical performance)

1. **Phase formation and stability are influenced by not only chemistry but also processing conditions**
2. **Effects of alloying additions on phase formation, stability and properties are not as simple as expected**

Phase formation in the as-cast FeCoNiCrMn

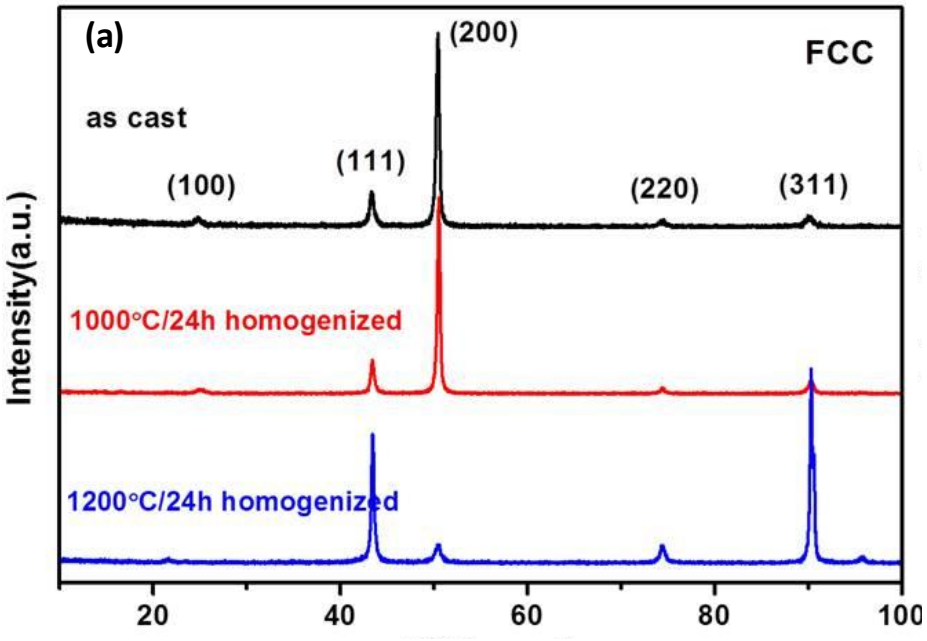


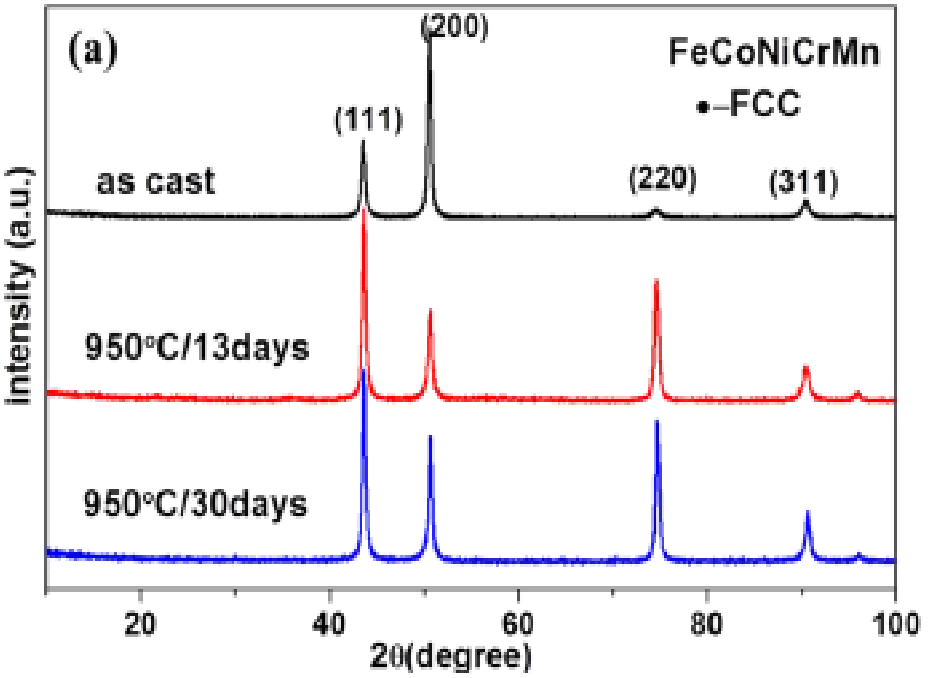




- Basically the alloy has a single fcc phase but with a small fraction of unidentified phase (Cr_2Mn oxide ?)

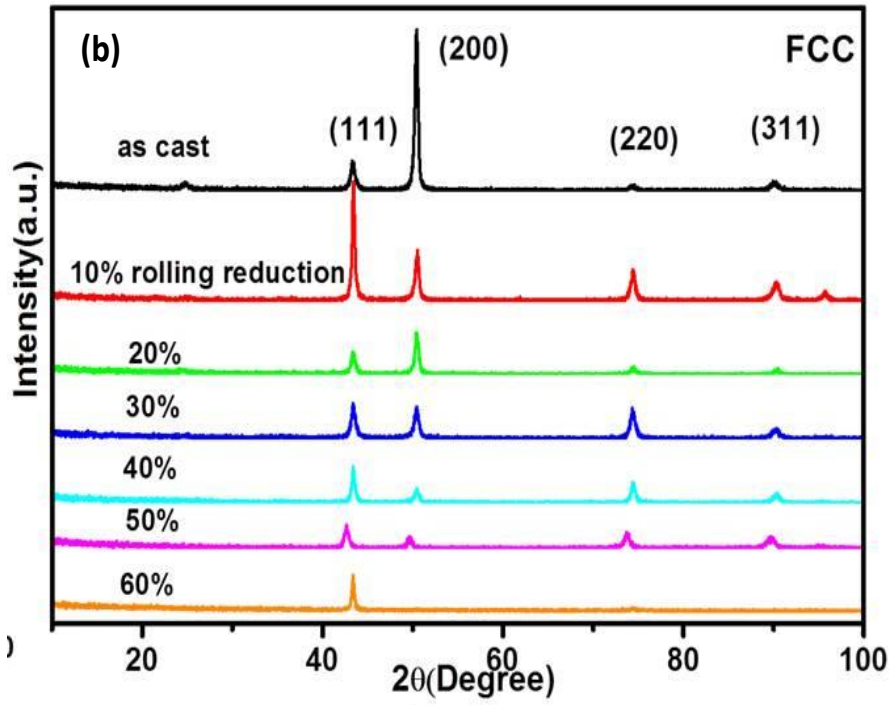
The FeCoNiCrMn high entropy alloy showed high phase stability

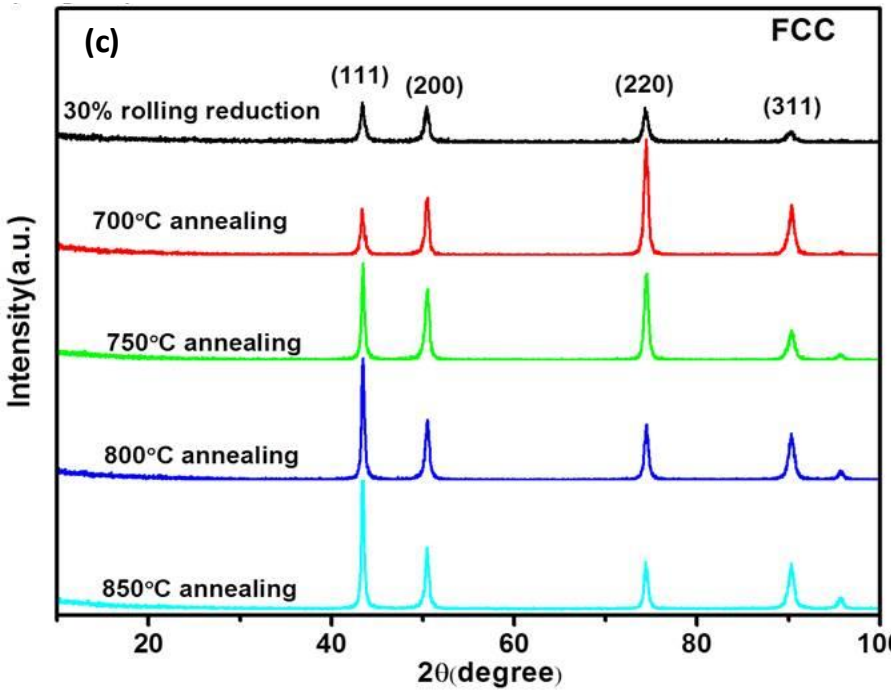




➢ The single fcc phase in the FeCoNiCrMn alloy is stable even after 30 days annealing at 950 °C

The FeCoNiCrMn high entropy alloy showed high phase stability





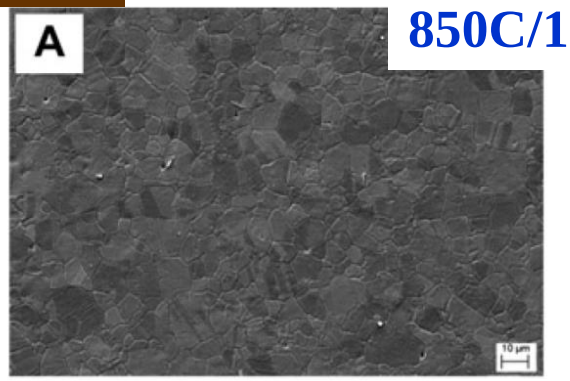
- Texture seems changed with the processing conditions
- No second phase was formed during the rolling/annealing processes

Content

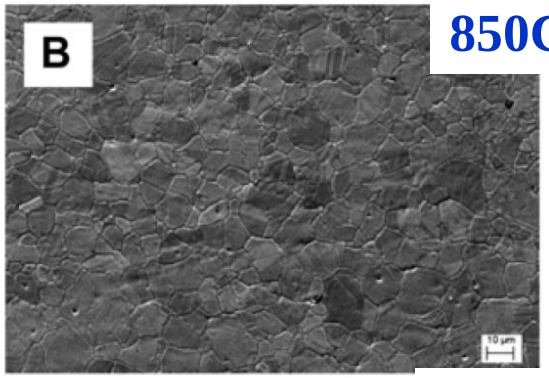
- Phase formation and stability
- Grain growth at elevated temperatures
- Deformation behavior
- Alloying effects

Grain growth behavior of the FeCoNiCrMn high entropy alloy was studied in detail

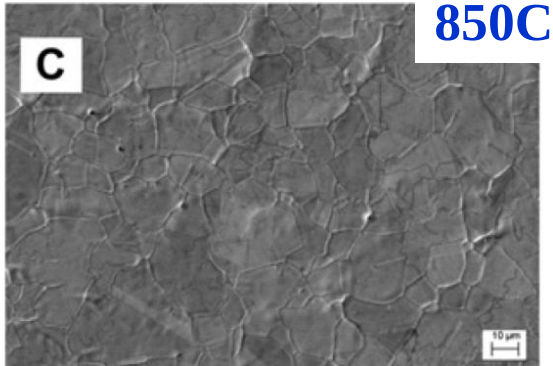
70% cold rolled



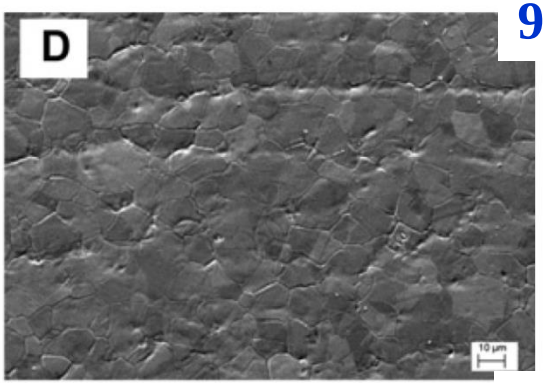
850C/1h



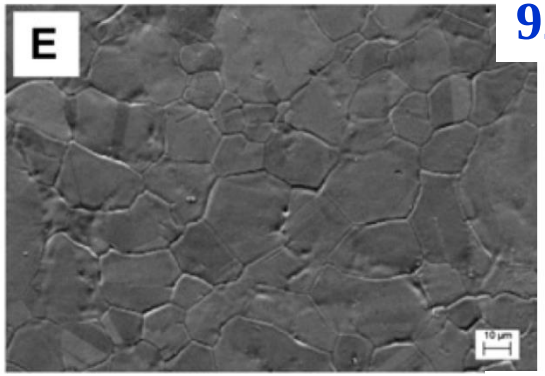
850C/2h



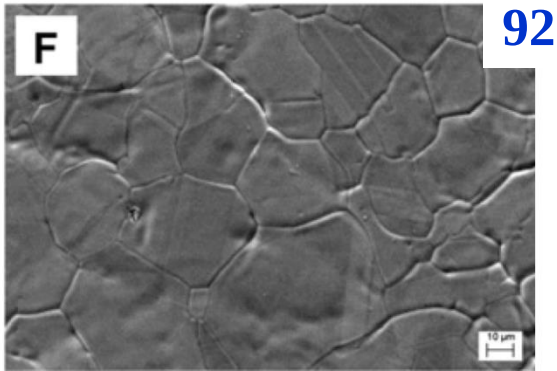
850C/2h



925C/1h



925C/2h



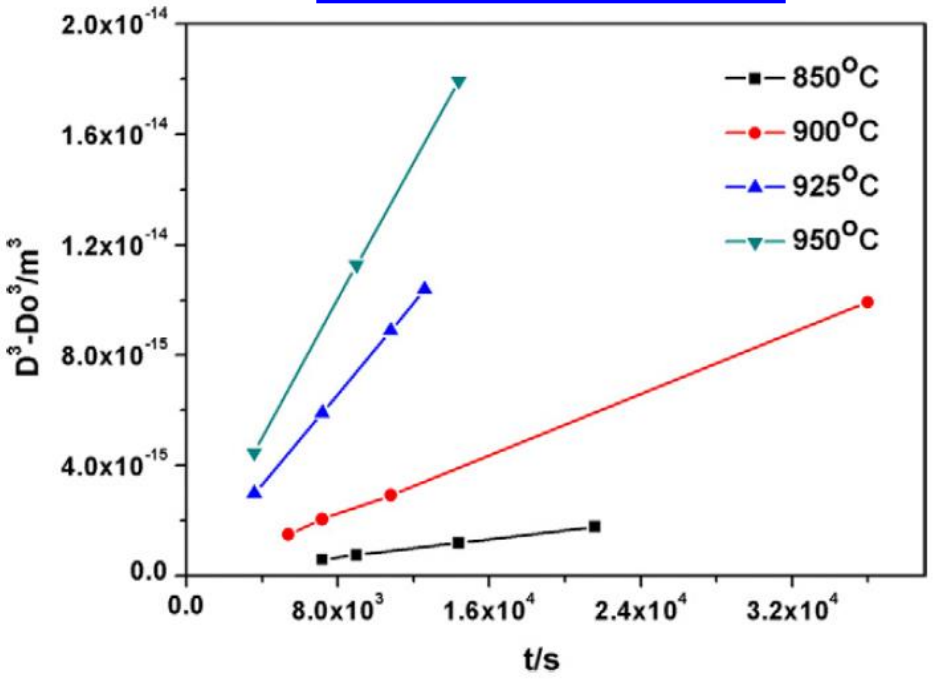
925C/3.5h

Grain coarsening exhibited a classical power law behavior in the FeCoNiCrMn alloy

Table 1. Grain sizes of the FeCoNiCrMn samples annealed at 850, 900, 925 and 950 °C for different time periods.

Temperature (°C)	Time (h)	Grain size (μm)
850 °C	1	3.9
	1.25	5.7
	1.5	6.5
	1.75	7.2
	2	8.4
	2.5	9.0
	4	10.6
	6	12.1
900 °C	0.5	5.2
	1	6.9
	1.25	9.0
	1.5	11.4
	2	12.7
	3	14.3
	10	21.5
925 °C	1	14.4
	2	18.1
	3	20.7
	3.5	21.8
950 °C	1	16.5
	2.5	22.4
	4	26.2

$$D^n - D_0^n = Ct$$

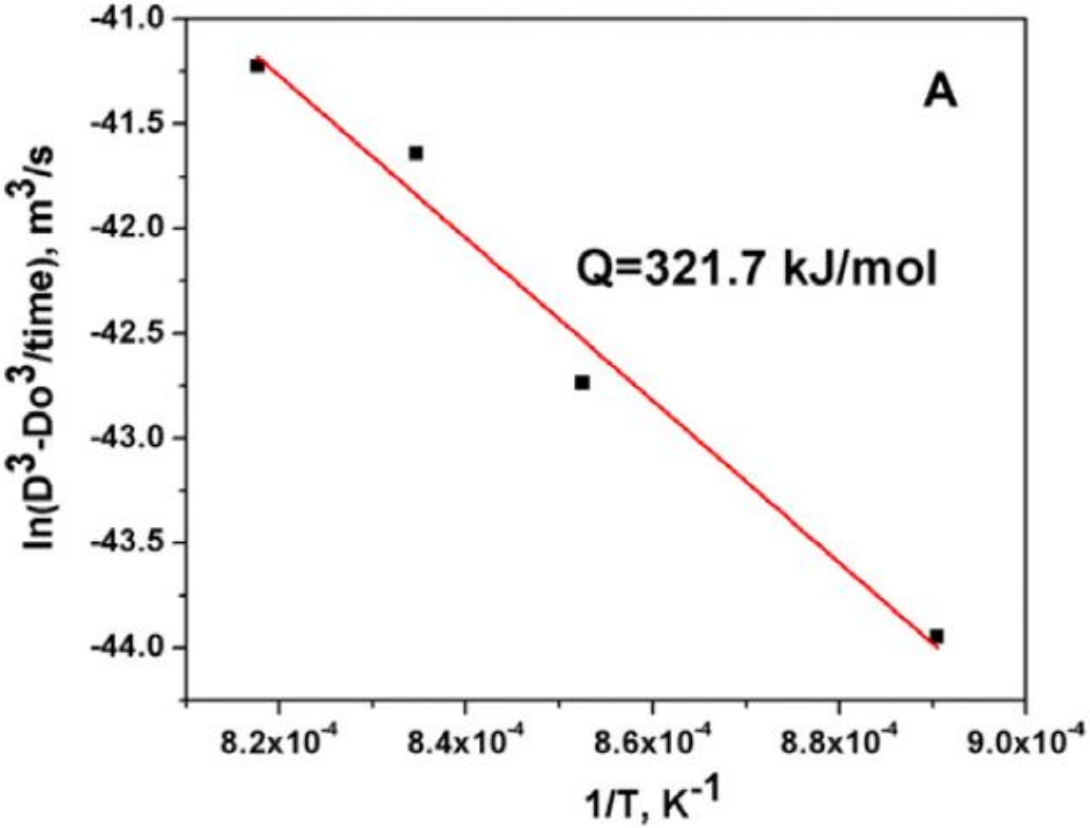


- n = 3 and D_0 = 1.0 μm
- n is larger than 2 which is for the "ideal" grain growth in single-phase pure materials

Liu et al., Scripta Materialia 2013;68:526

The apparent activation energy for grain growth suggests that sluggish diffusion indeed occurred

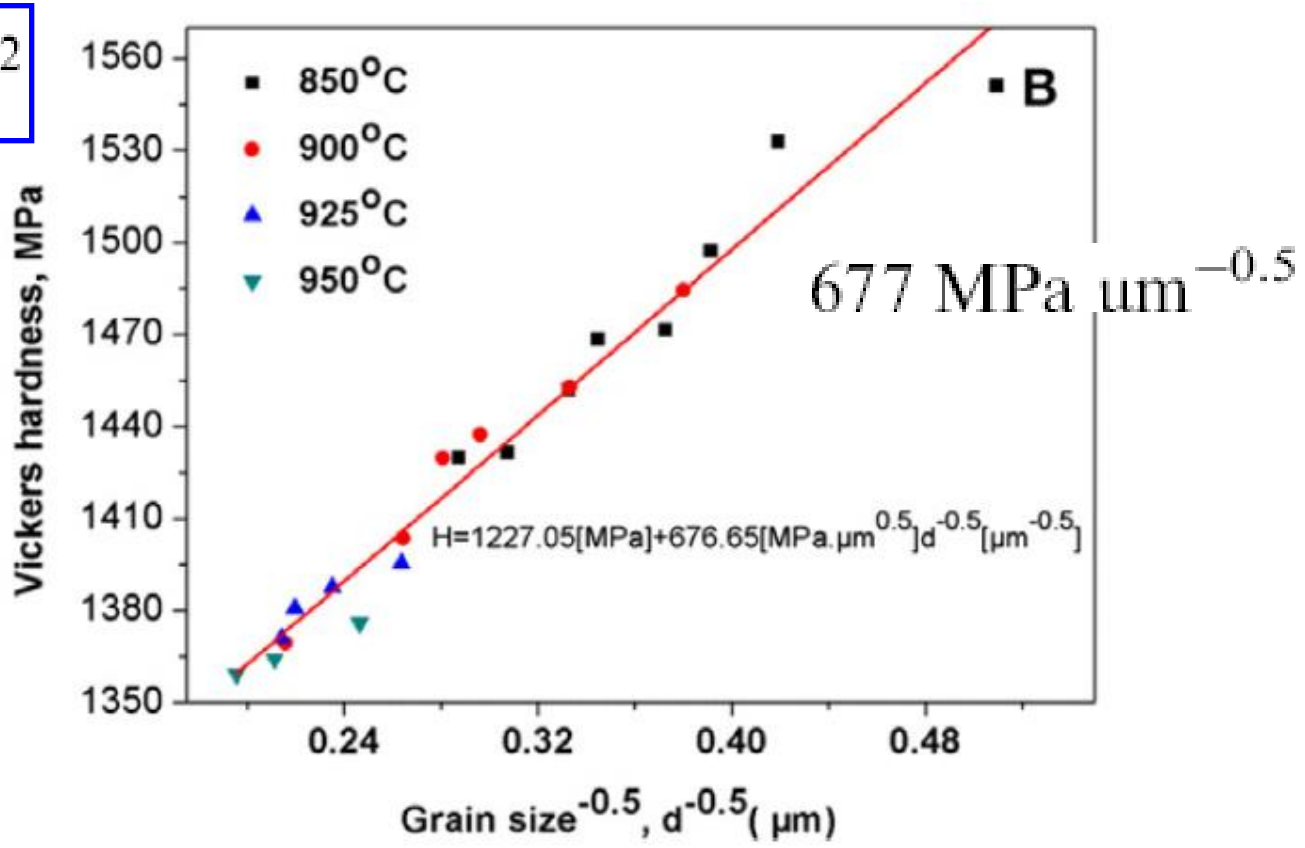
$$C = A_0 \exp(-Q/RT)$$



- The Q value is much higher than that for AISI 304LN stainless steels, which is only about 150 kJ mol^{-1}

The hardness values at different temperatures closely follow the classical Hall–Petch relationship

$$H = H_0 + k_{HP} d^{-1/2}$$



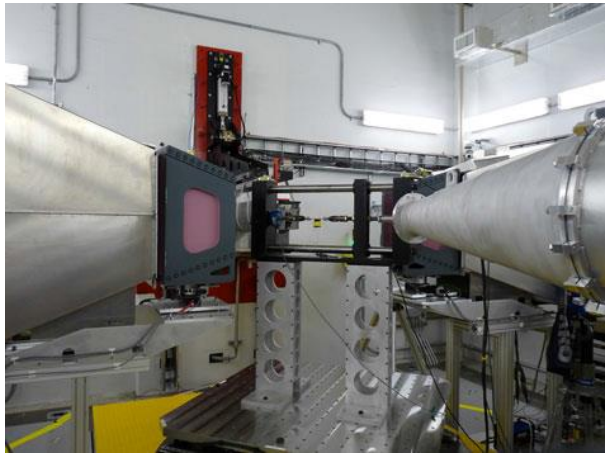
- The softening mainly from grain coarsening
- The K_{HP} is larger than 600 Mpa μm$^{-0.5}$ (the upper-bound for fcc metals) , suggesting that grain boundary hardening efficiency is obviously higher

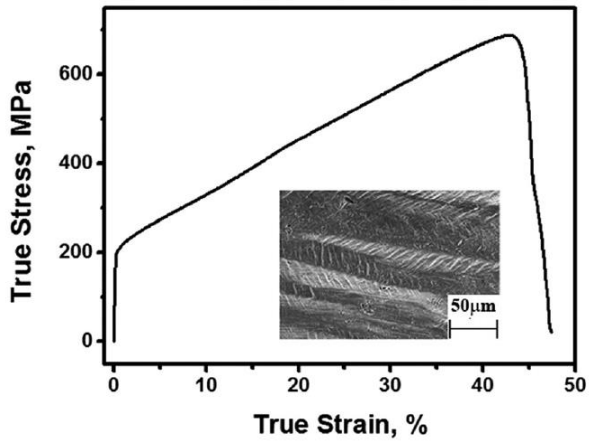
Content

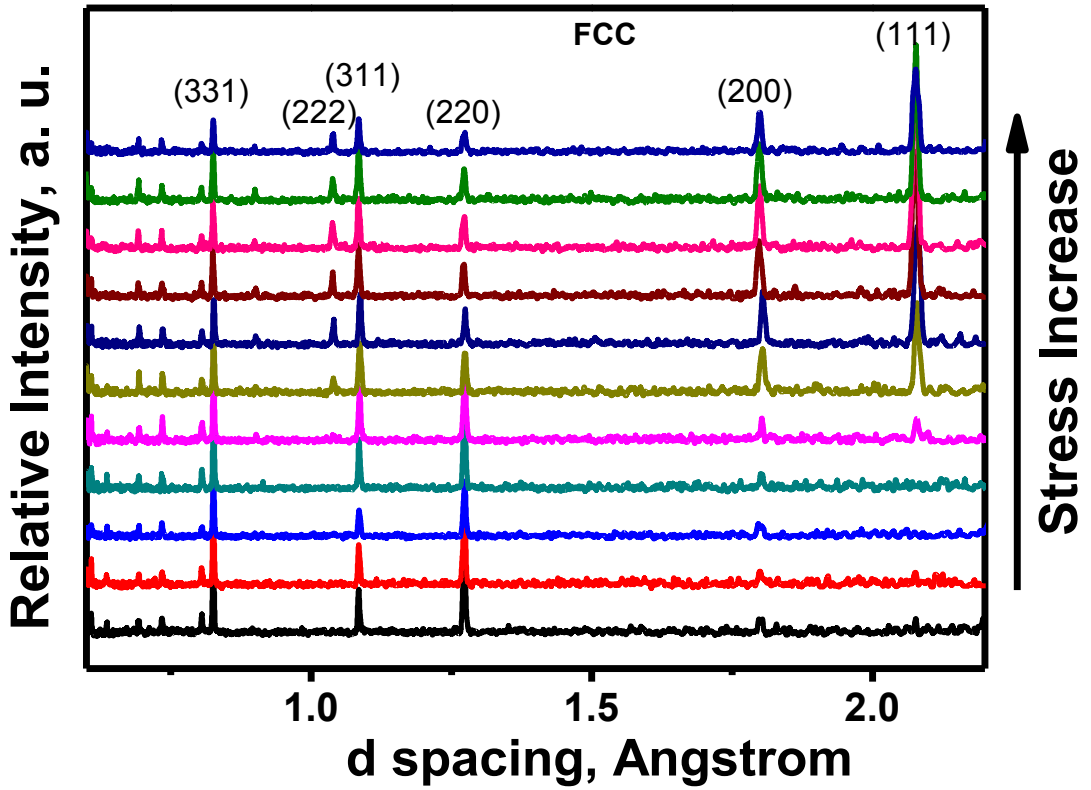
- Phase formation and stability
- Grain growth at elevated temperatures
- Deformation behavior
- Alloying effects

In-situ neutron diffraction study of deformation behavior of the FeCoNiCrMn alloy was conducted

VULCAN system at Spallation Neutron Scattering, Oak Ridge National Laboratory

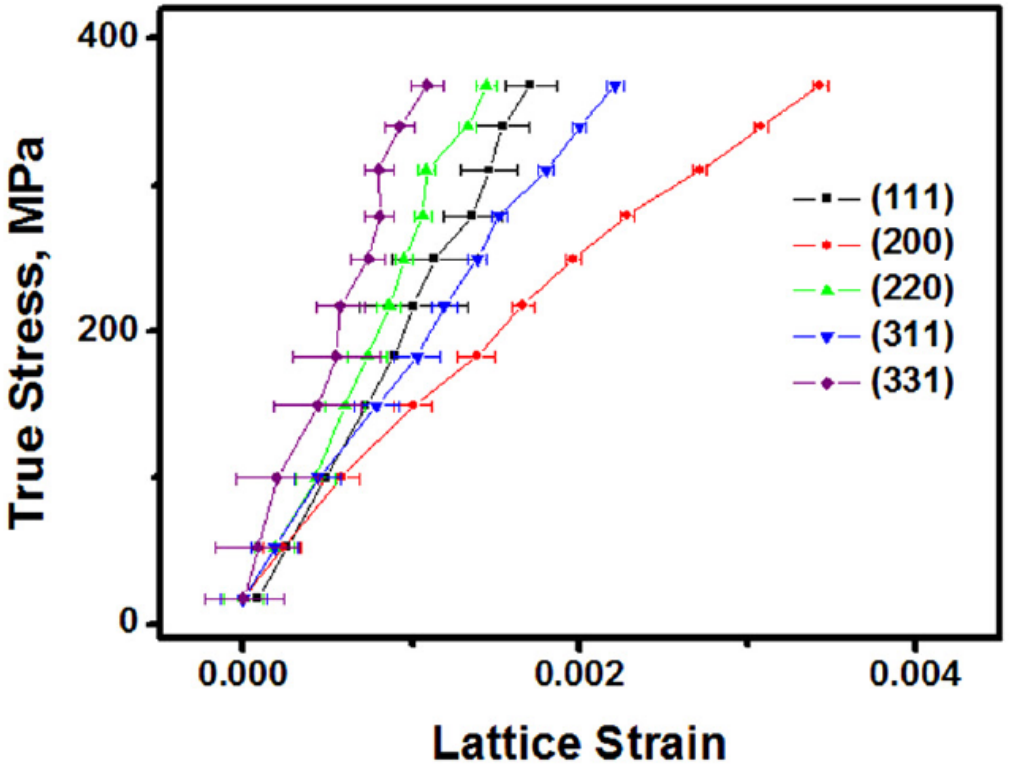






Wu et al., Appl. Phys. Letts. 2014;104:051910

Strong elastic anisotropy was observed during the tensile loading

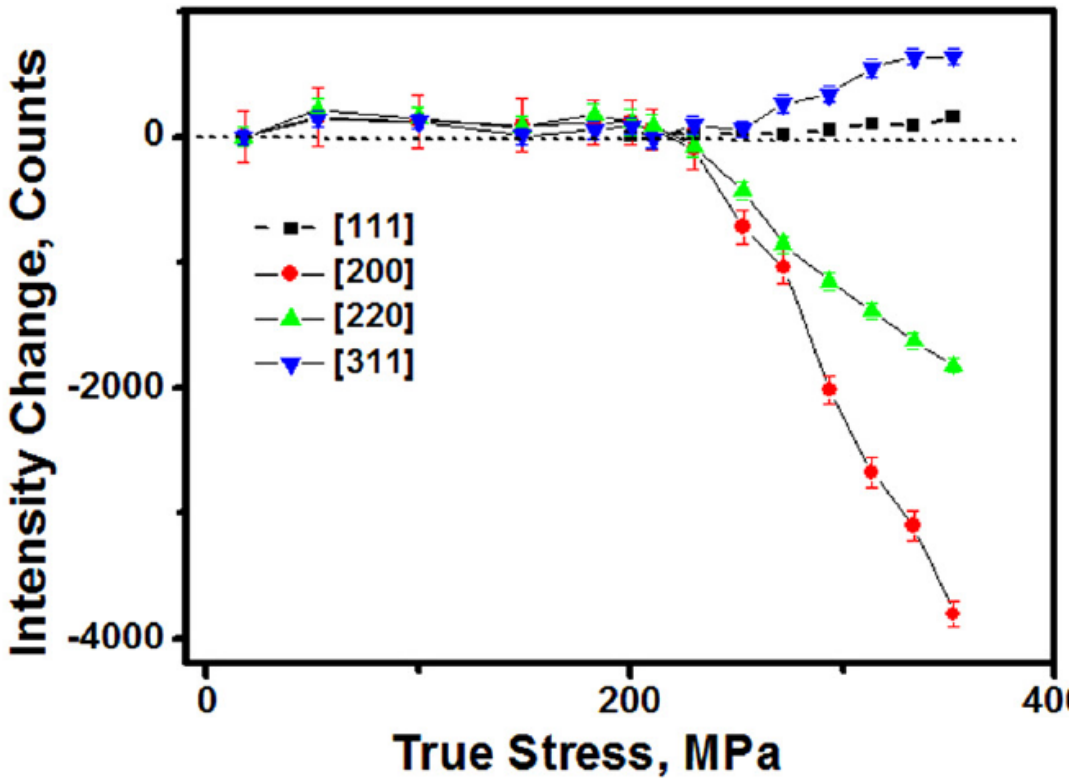


- The lattice strain change is strongly dependent on the grain orientations
- The {200} planes have the lowest elastic modulus while the {331} planes have the highest
- Young's modulus anisotropy ($E_{[111]}/E_{[100]}$) is 1.98, close to that of Ni (2.17) but smaller than that of typical fcc steels (3.20)

Modulus: GPa

$E_{[200]}$	$E_{[220]}$	$E_{[111]}$	$E_{[311]}$	$E_{[331]}$
112.2	223.2	222.6	163.5	266.7

Development of a textured structure during the tensile deformation

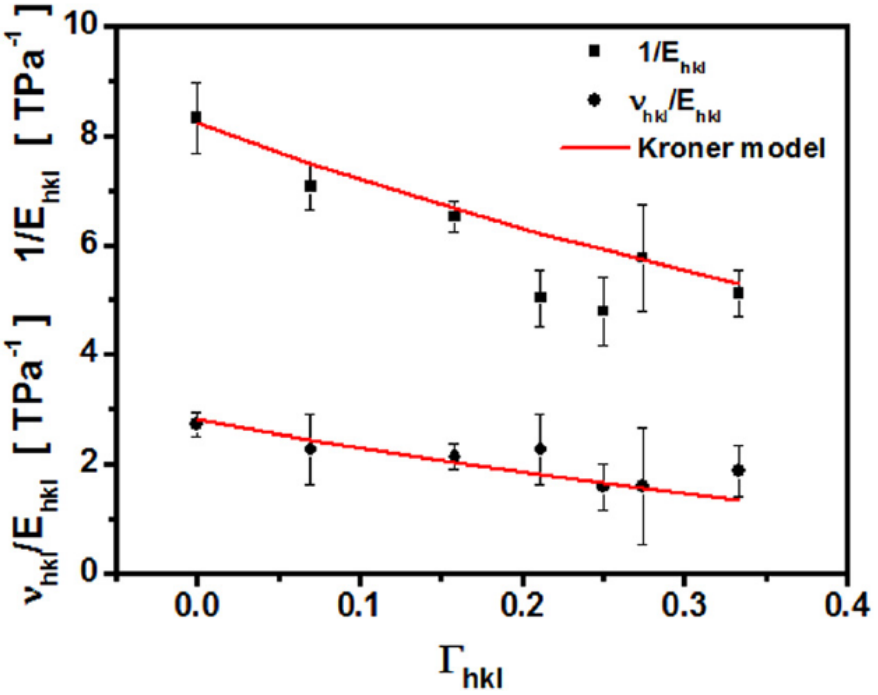


- The peak intensity of the {220} and {200} reflections decreased, while that of the {111} reflections increased
- Textural evolution of the current HEA during tension appears to be similar to those of typical FCC metals and alloys, for example, polycrystalline copper with columnar grains

The single crystal elastic constants of the current HEA were determined by the Kroner's model

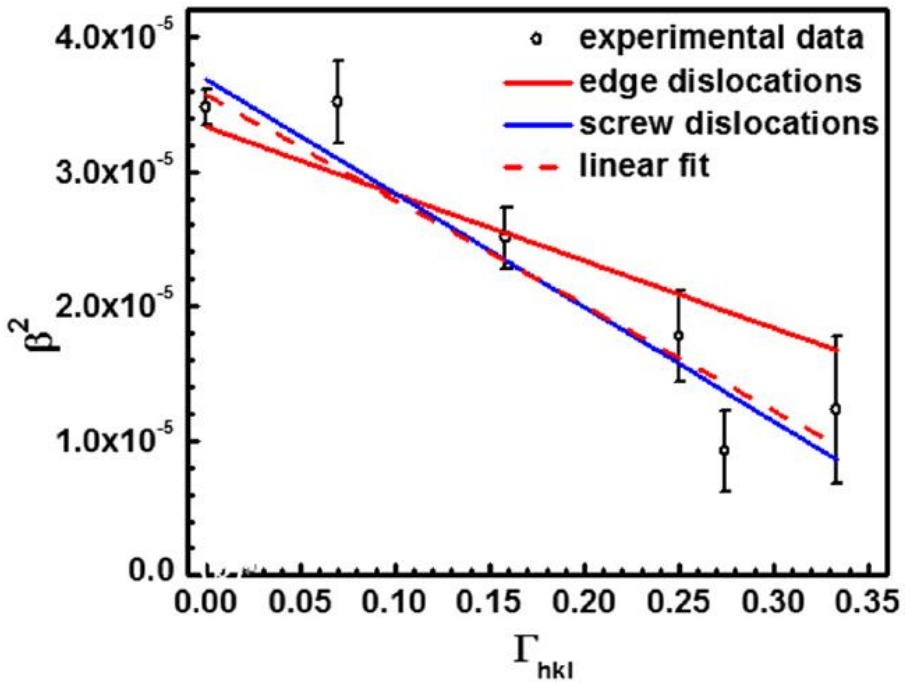
The cubic elastic anisotropy factor

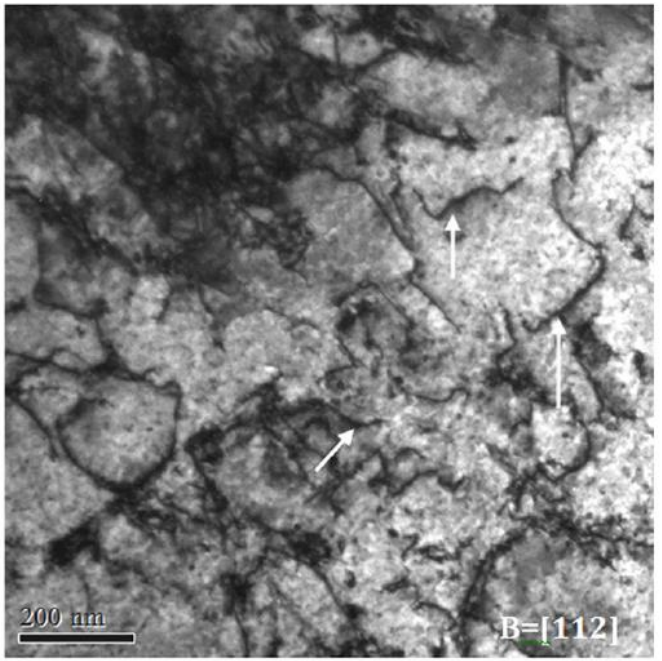
$$\Gamma_{hkl} = \frac{h^2k^2+k^2l^2+l^2h^2}{(h^2+k^2+l^2)^2}$$



- **The shear anisotropy was calculated as 2.84, much smaller than that of the ternary FeCrNi alloy (3.77), but close to that of the pure FCC-Ni (2.51), manifesting that the elastic anisotropy behavior of the current HEA is close to that of its FCC component, i.e., pure Ni.**

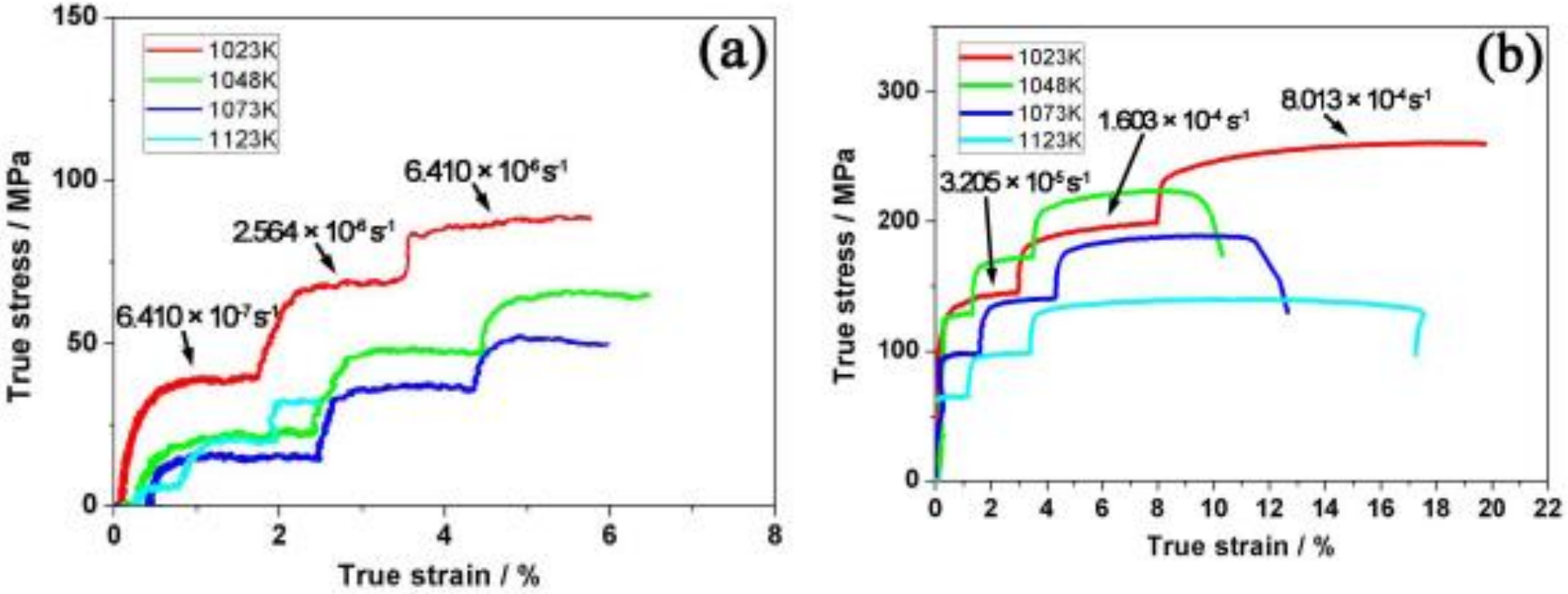
The experimentally determined peak broadening data can reveal the dislocation types during deformation





- The slope in the above plot is 2.189, which seems like a balancing value for the edge (1.492) and screw (2.298) dislocations, but close to that of the <110> screw dislocation
- A representative bright field image with wiggled dislocations in a deformed specimen, suggesting a mixed dislocation characteristics

Flow behavior at different temperatures and strain rates were investigated



He et al., Intermetallics 55, 2014; 9-14.

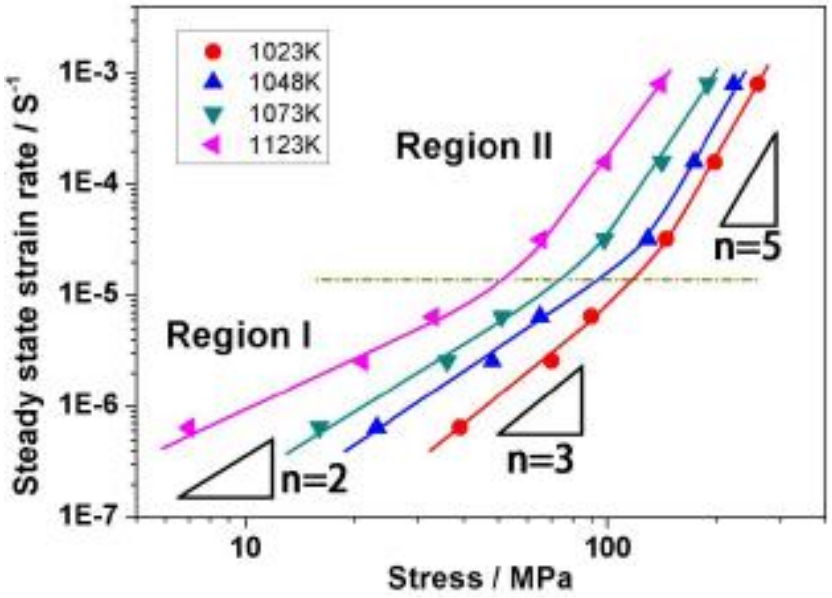
- The temperature is in between 1023 and 1123 K
- The strain rate ranges from 6.410×10^{-7} to 8.013×10^{-4} s^{-1}

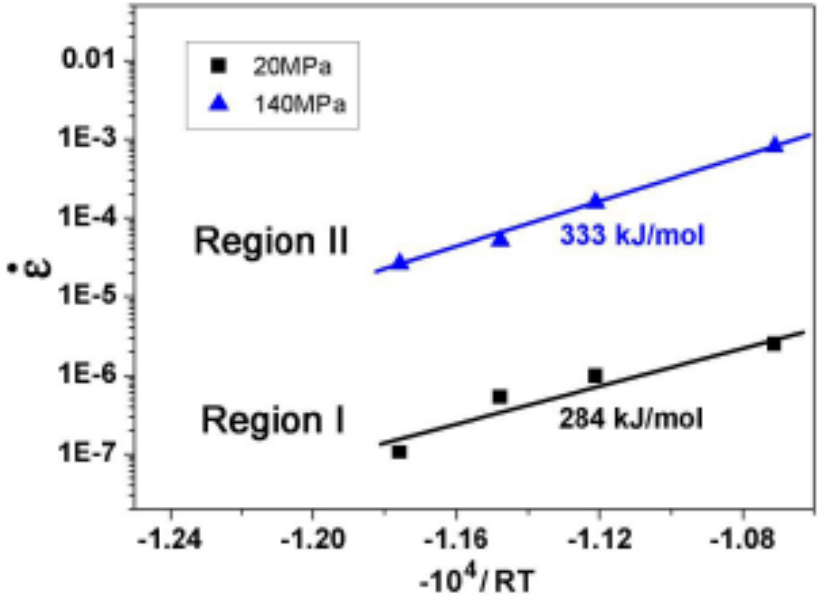
Steady-state deformation behavior of FeCoNiCrMn

The Norton Equation

$$\dot{\varepsilon} = A\sigma^n$$

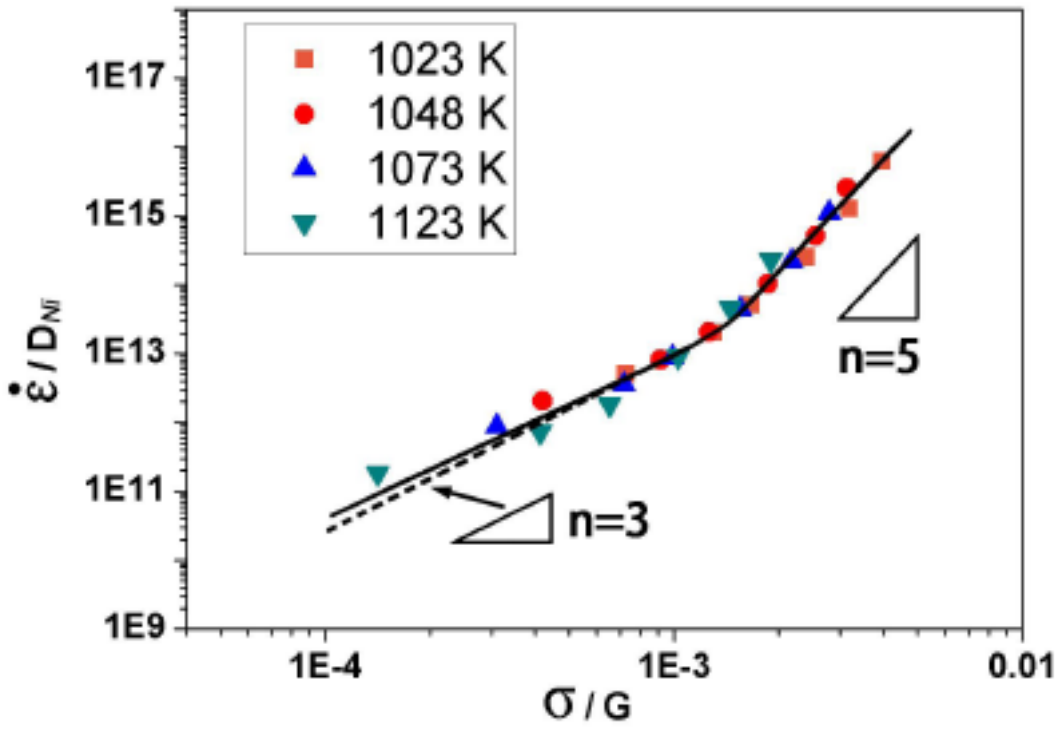
$$\dot{\varepsilon} = A'\sigma^n \exp(-\frac{Q}{RT})$$





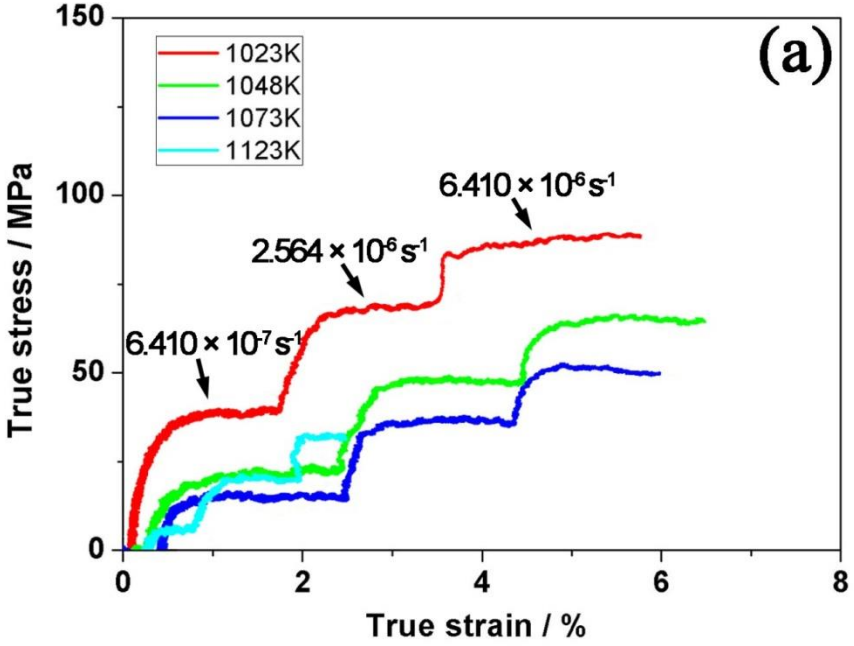
- Region II with a high stress exponent at the high strain rates (or stresses) while Region I with a low stress exponent at the low strain rates (or stresses)
- The activation energy in two regions are comparable to that for lattice diffusion. For example, Ni (317.5 kJ/mol), Cr (292.9 kJ/mol), and Mn (288.4 kJ/mol)

The normalized plot indicates that the data obtained at various temperatures (1023-1123 K) collapse into one single master curve



- In the high strain rate regime, n is ~5 and the activation energy is ~330 kJ/mol, suggesting a dislocation-climb mechanism and the slowest diffusing species Ni controls the rate process.
- In the low strain rate regime, n is <3 and the activation energy is ~ 280 kJ/mol, suggesting that the mechanism is the dislocation gliding and the deformation rate is controlled by the diffusion of one of the constituent elements which acts as the solute atom.

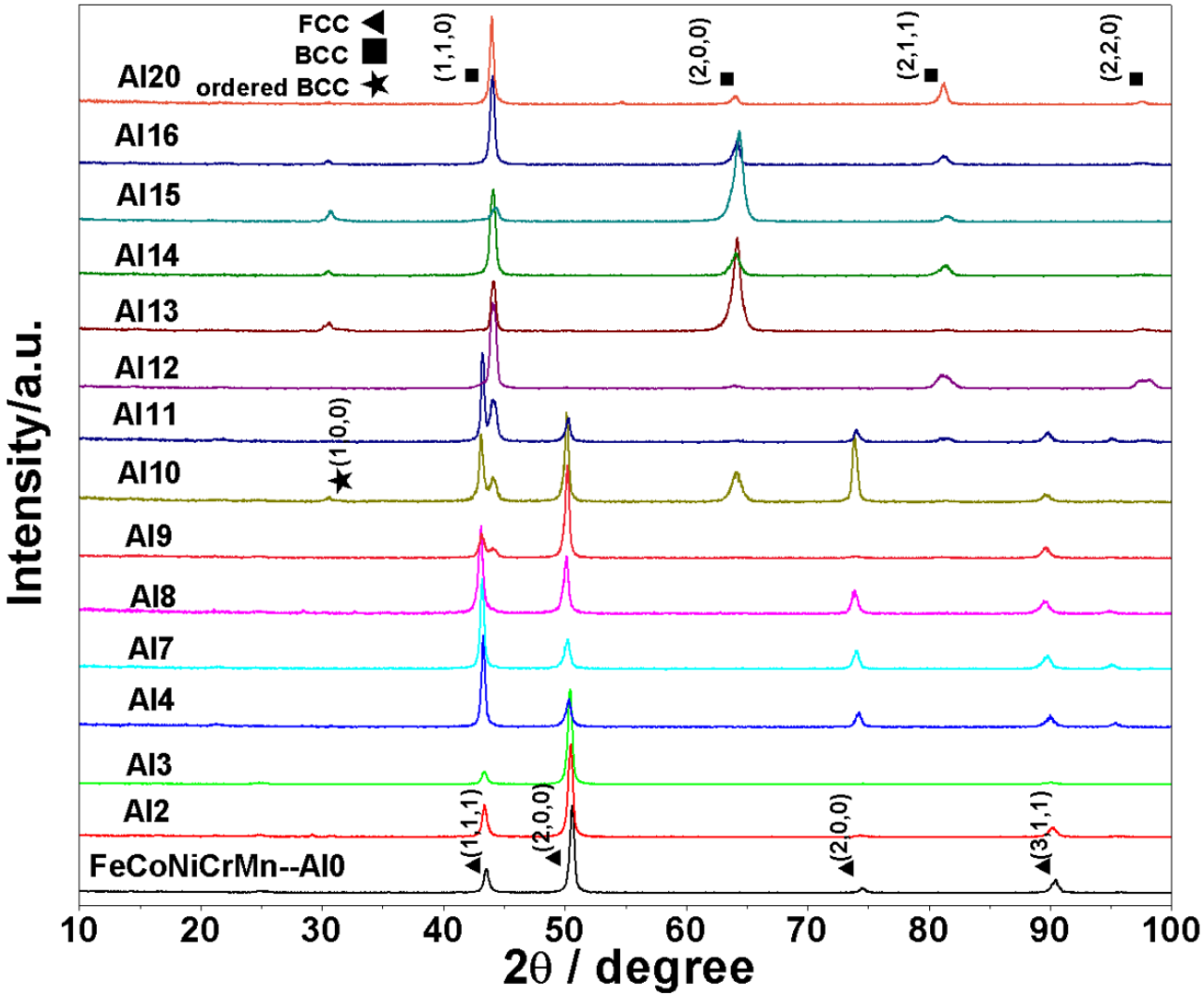
1. Relatively lower steady state flow stress than super alloys
2. Oxidation resistance is low due to highly active element Mn



Content

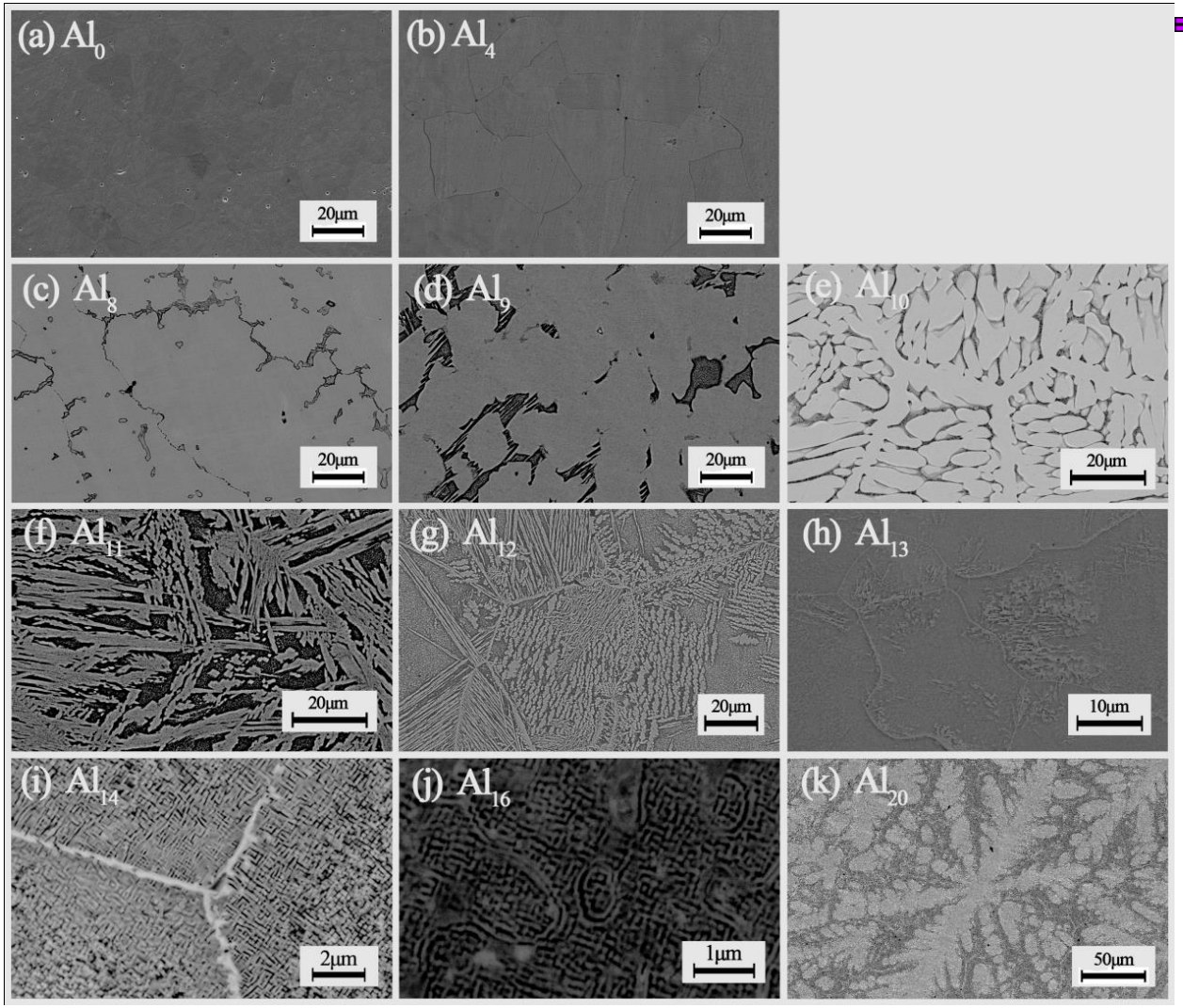
- Phase formation and stability
- Grain growth at elevated temperatures
- Deformation behavior
- **Alloying effects—Al effects**

Addition of Al in the $(FeCoNiCrMn)_{100-x}Al_x$ alloys induced a phase transition from fcc to bcc starting at Al8



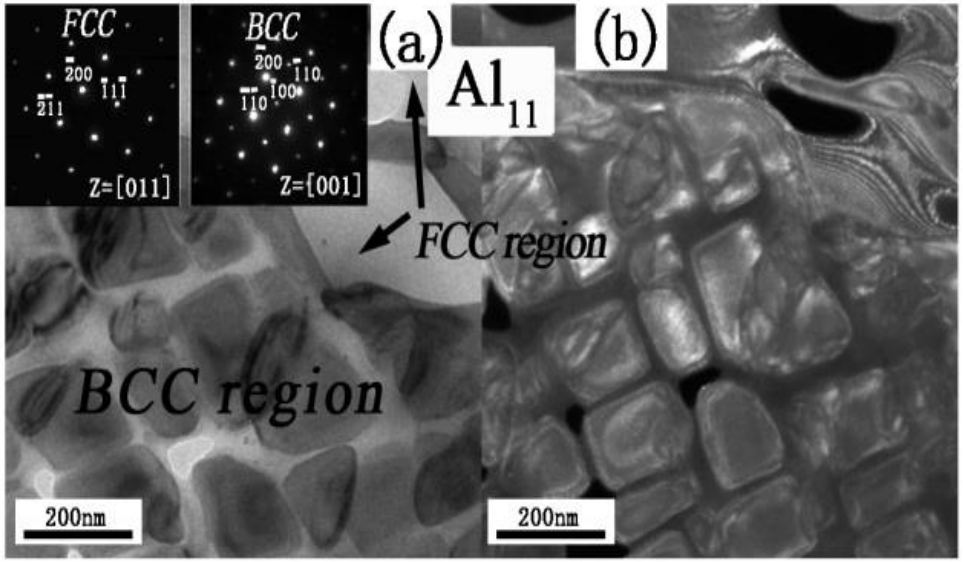
He et al., Acta Mater. 2014; 62:105.

Microstructure observation further confirms the phase transition resulted from the Al addition



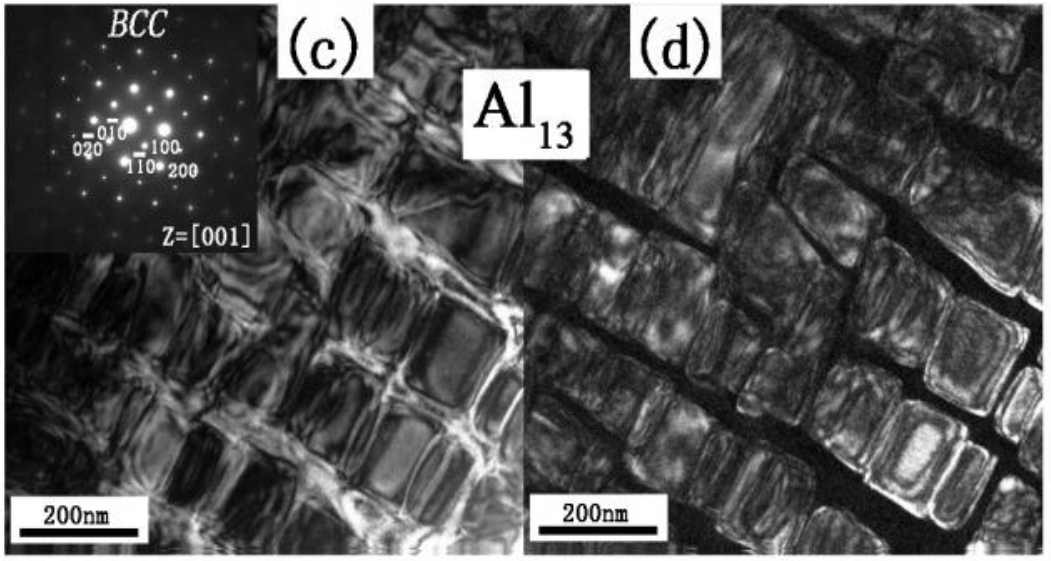
- Bcc phase becomes dominant in alloy Al13, Al14 and Al16 , and the minor fcc phase mainly lies in the bcc grain boundaries.

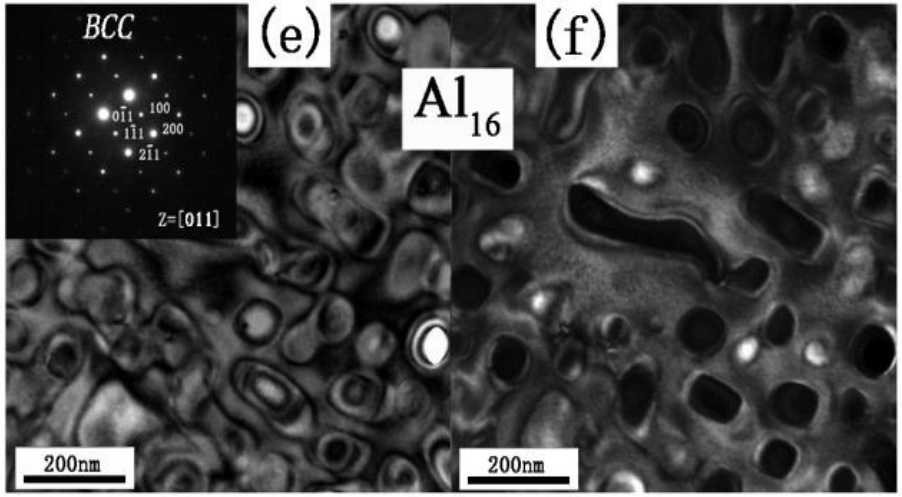
TEM characterization reveals the detailed phase characteristics



The cubic-shaped particles are ordered B2 while the inter-precipitate area is disordered A2. fcc: 74.6%.

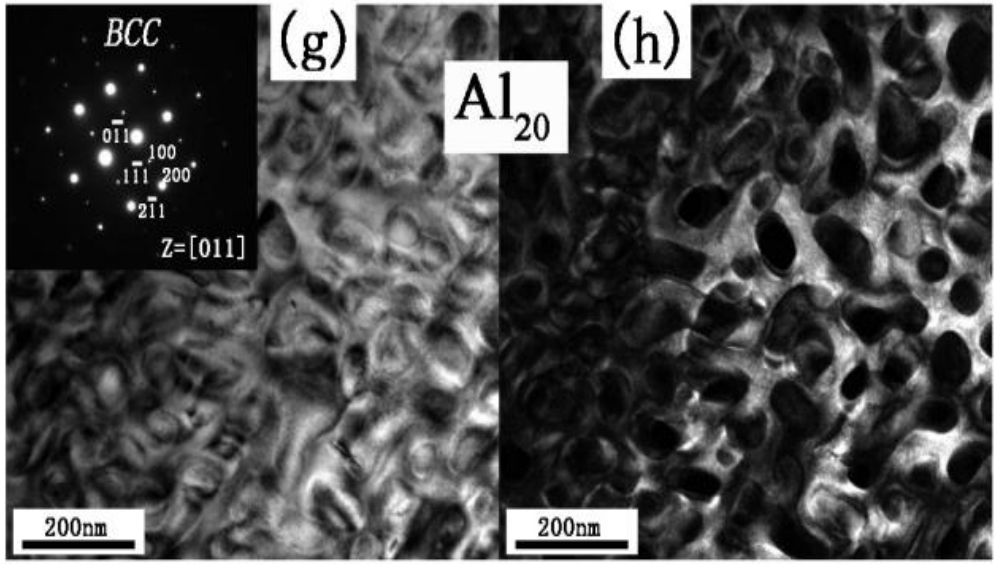
The cubic-shaped precipitates become slightly smaller but more close-packed. fcc: <20%



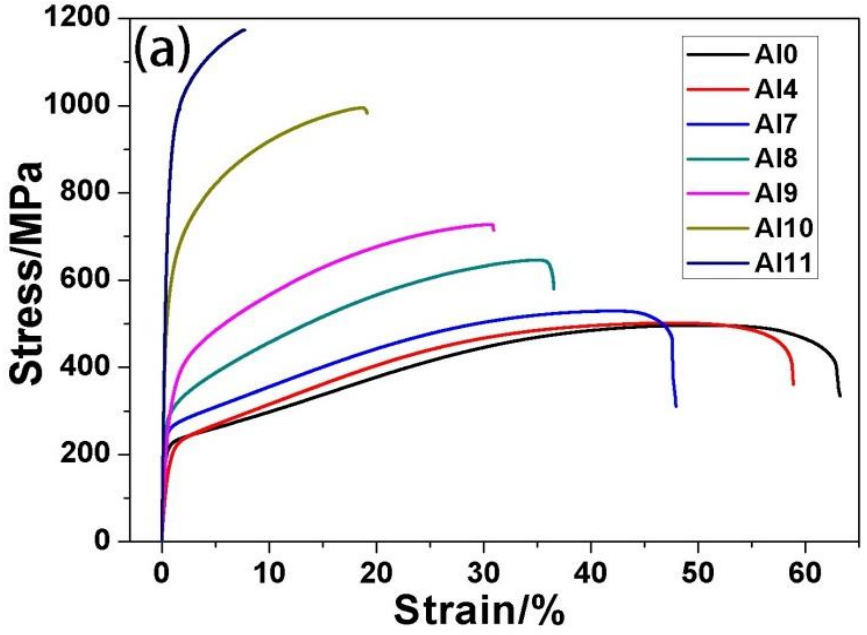


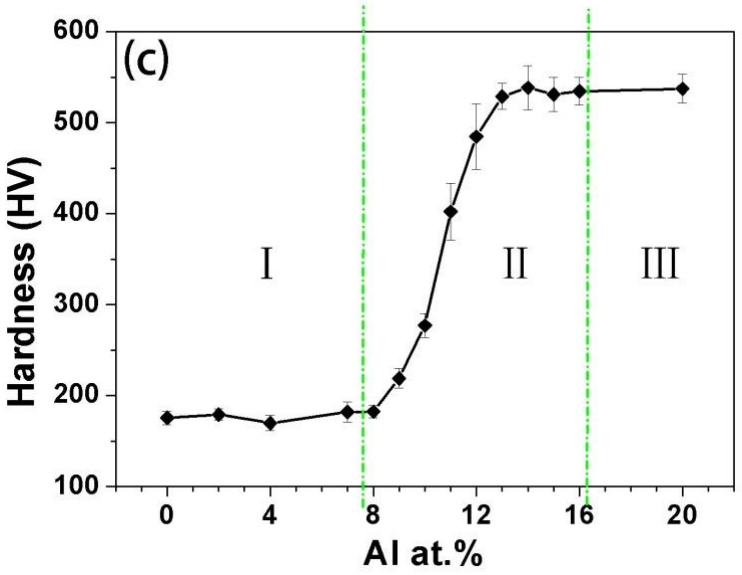
spherical A2 particles (～100 nm) embedded in the B2 matrix. Limited fcc phase existed only on the boundaries of the bcc grains.

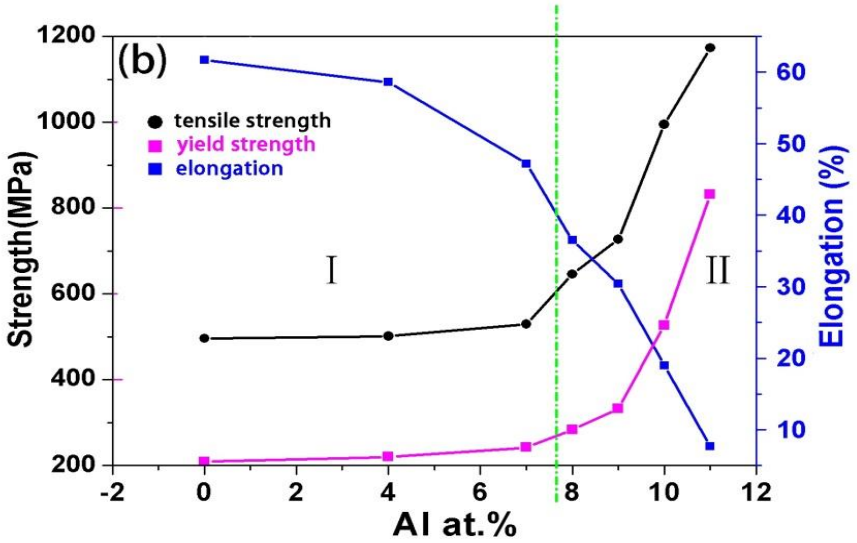
Similar to Al16, but the fcc particles disappear completely.



Tensile properties and hardness as a function of the added Al content

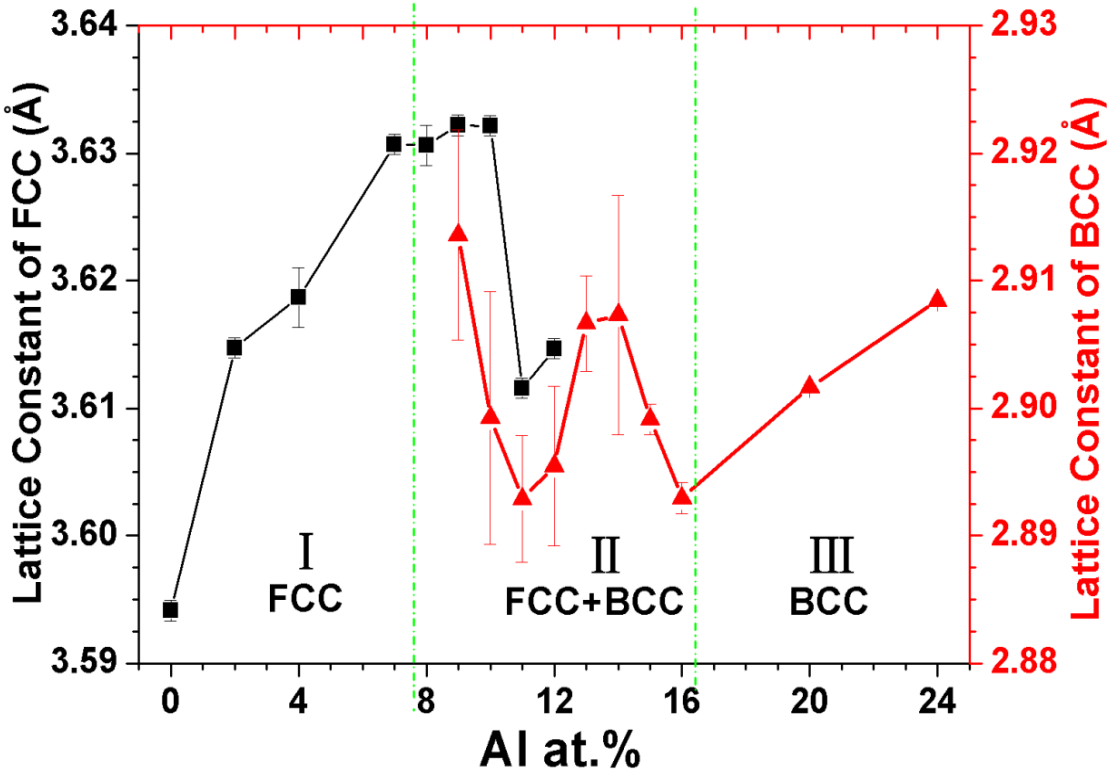






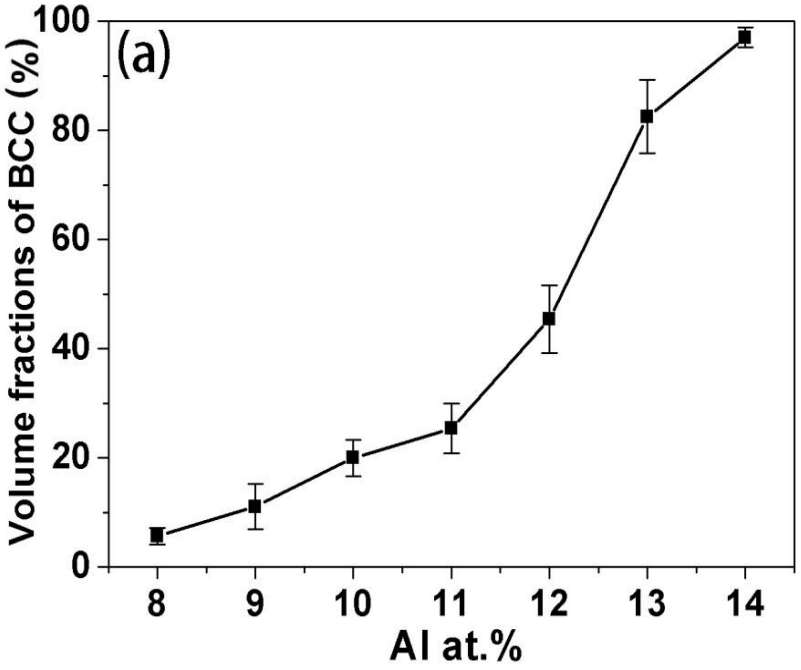
- Strength is increased but the ductility is decreased as Al is added
- The alloys became too brittle once Al exceeds 11%
- Hardness also sharply increases with the Al level and approaches 538 HV in Al14

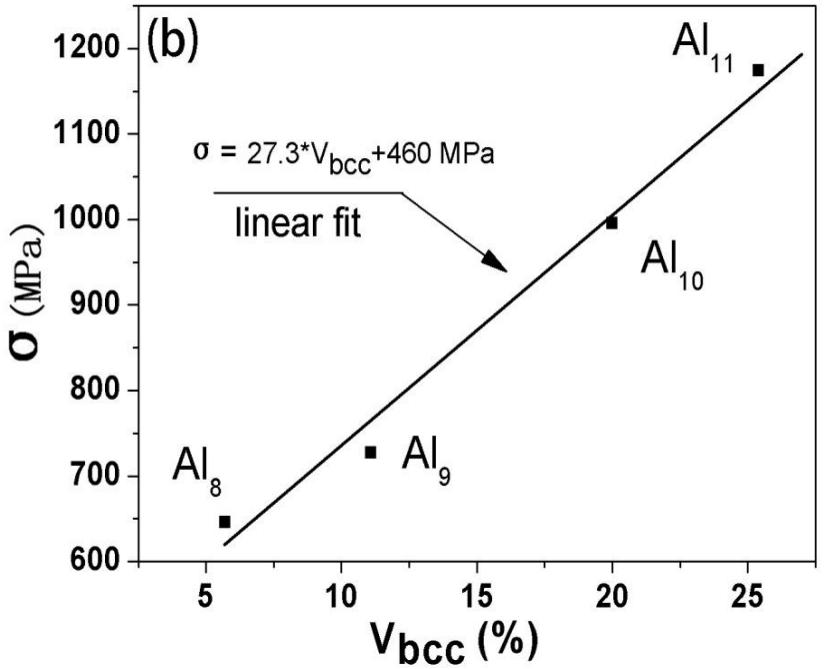
Change in the lattice constant can explain the tensile deformation behavior for the single fcc alloys



- Lattice constant is linearly increased with Al in region I, suggesting a solution strengthening effect caused by the enlarged lattice distortion

The tensile properties of the alloys with duplex structures can be explained by the simple rule-of-mixture





- The composite model offers reasonable interpretation for the strength increment of the alloys in region II.
- Al11 alloy have fracture strength of 1174 Mpa and tensile ductility of 7.7%.
- alloys with >11% Al are too brittle to be deformed due to formation of ordered BCC structures.

Summary

Phase formation and stability -- high (homogenization, long term aging, rolling)

Grain growth at high temperatures --slow

Al effects -- solution strengthening

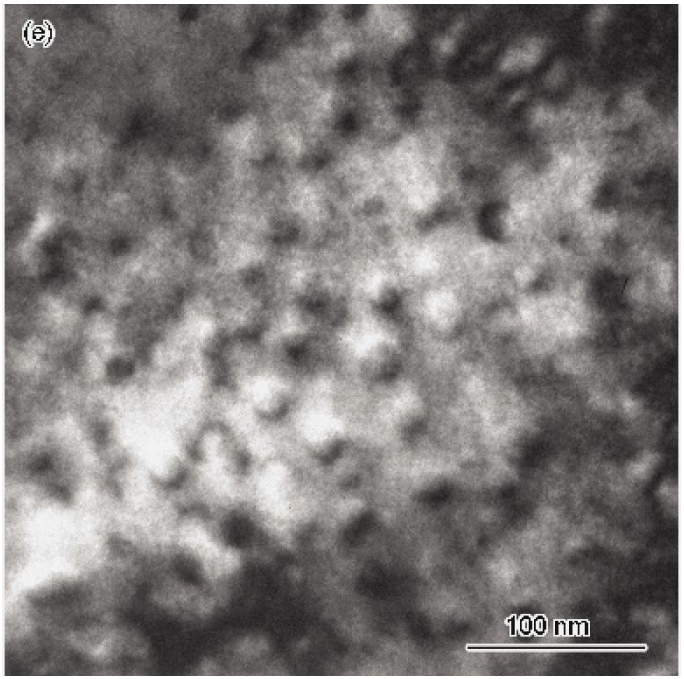
FeCoNiCrMn alloy

Deformation behavior --
RT: similar to Ni, mix dislocations
HT: high strain rate, dislocation climb
low strain rate, dislocation glide

High-T materials

Hardening mechanisms urgently needed in the FeCoNiCr HEA system

- Secondary phase hardening resulted from bcc phases (NiAl B2) in FeCoNiCrMn is not very satisfactory.
- Based on previous studies in steels and superalloys, L12 phase (**γ' phase-Ni_3Al)** is a desirable secondary phase for a fcc matrix, both at room and elevated temperature.



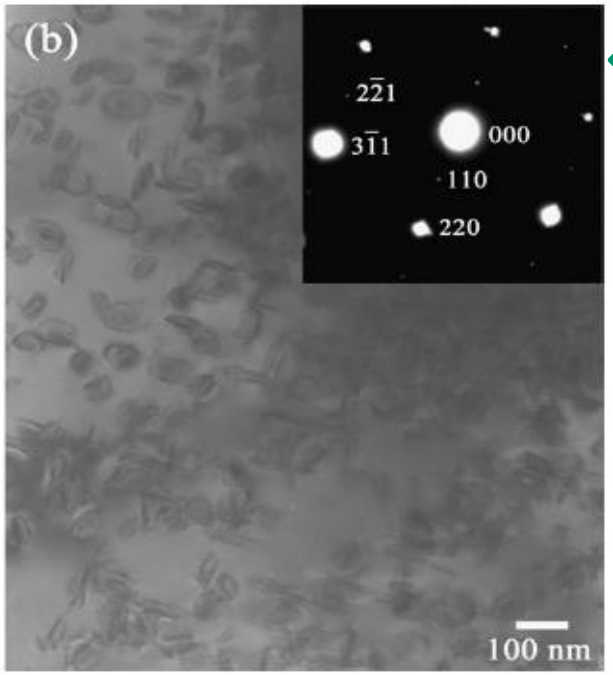
GH984G合金中球形Ni_3Al型γ′沉淀相颗粒

金属学报，1978,14(3) :227-237

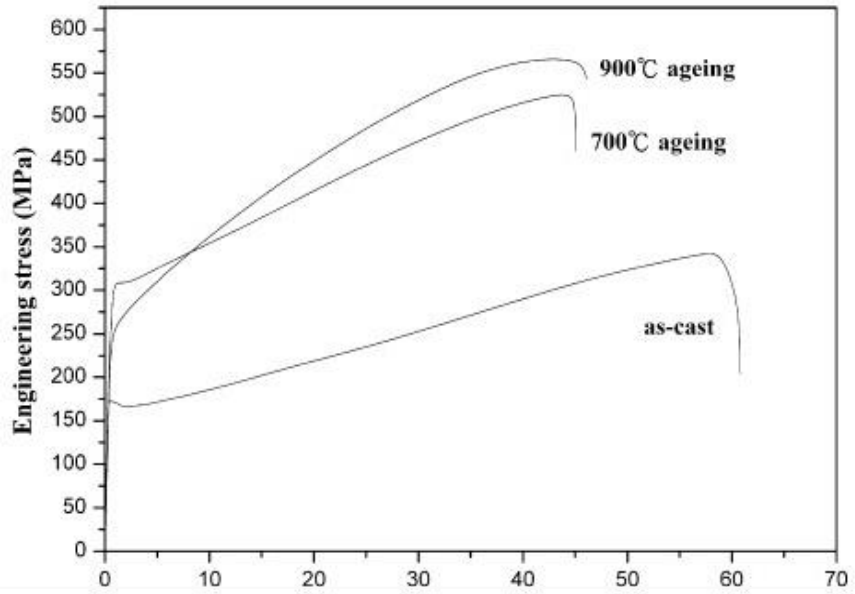
金属学报. 2014, 50(10): 1260-12

Addition of Al alone cannot effectively promote precipitation of a large density of nanosized γ' particles uniformly dispersed in the matrix

Shun TT et al. JAC 2009;479:157–160



The L12 precipitates was observed in the fcc $Al_{0.3}FeCoNiCr$



- **The tensile strength is only increased slightly after aging due to the fact that the γ' precipitates distribute inhomogeneously.**
- **More work has been done for γ' precipitation in HEAs.**

Unsolved scientific problems/ Key research topics

- Phase formation and stability
(why solid-solutions & under what conditions, phase transition, enthalpy effects, etc.)

- Alloy design and preparation
(alloying effects, structures & properties optimization, processes, etc.)

- Deformation mechanism and mechanical properties

- Physical and chemical properties

- Applications: different service temperatures