

**CEC/ICMC 2015**

**CrMnFeCoNi High Entropy Alloys prepared  
by Combustion Synthesis under High Gravity**

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# Outline

## **1. Introduction**

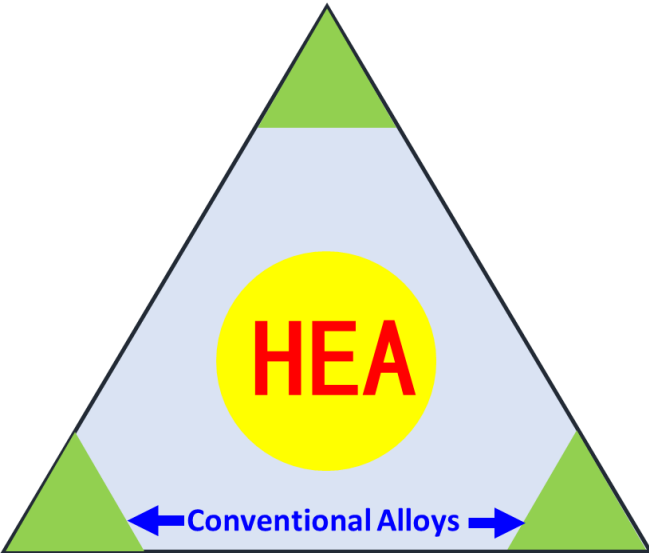
## 2. Experimental

## 3. Results and discussion

## 4. Conclusions

# High Entropy Alloys (HEA)

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HEA: equiatomic, multi-element systems that crystallize as a single phase, despite containing multiple elements with different crystal structures.

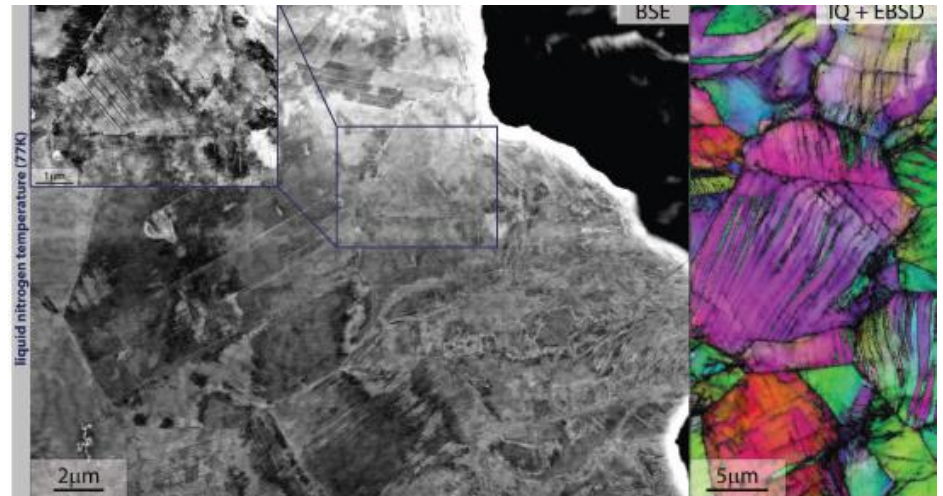
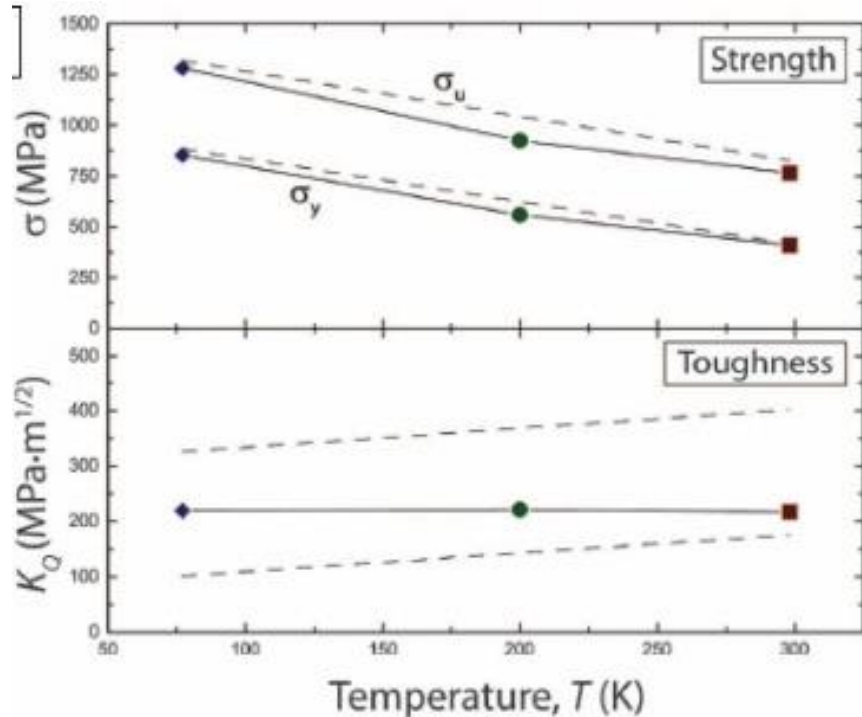
$$G = H - TS, \quad S \uparrow \rightarrow G \downarrow$$

The configurational entropy contribution to the total free energy in alloys with five or more major elements may stabilize the solid-solution state relative to multiphase microstructures.

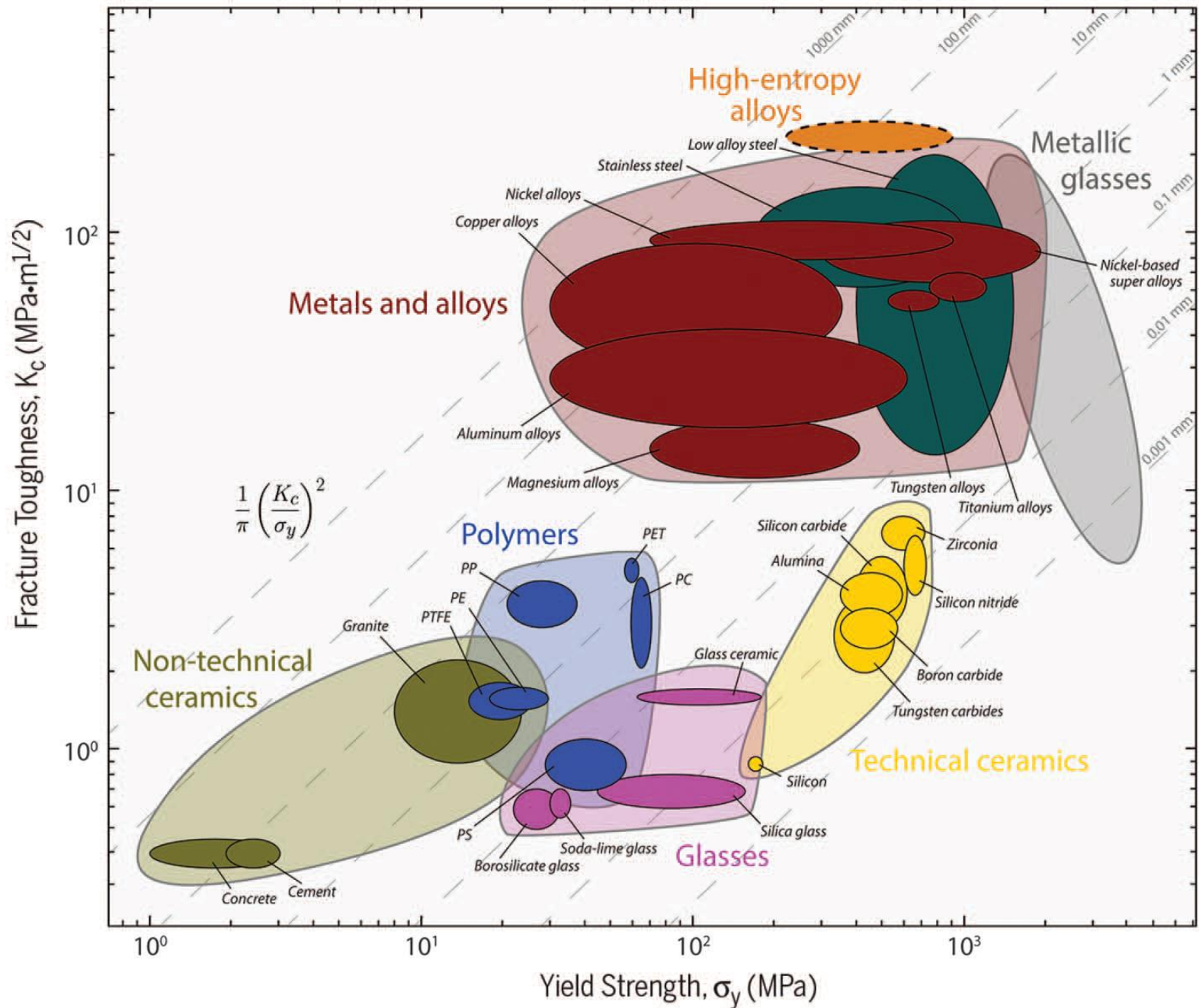
**The microstructure of HEA is often characterized with lattice distortion and nano-precipitates, which contributes to interesting mechanical properties.**

# CrMnFeCoNi HEA: Improved properties at Low T

The mechanical properties of CrMnFeCoNi HEA actually improve at cryogenic temperatures. This is attributed to a transition from planar-slip dislocation activity at room temperature to deformation by mechanical nanotwinning with decreasing temperature, which results in continuous steady strain hardening.



Bernd Gludovatz et al. Science 345, 1153 (2014)



# Preparation of HEA



Arc melting

1. Excessive Mn  $\rightarrow$  to compensate the loss of Mn by evaporation;
2. Pure Zr  $\rightarrow$  to remove oxygen;
3. Iterative melting for 5 times  $\rightarrow$  to improve the homogeneity



Induction melting

**Much time and energy consumption  $\rightarrow$  low efficiency**

# Challenge for preparation of HEA

1. Very different melting points ( $T_m$ ) of elements → How to depress the evaporation of low- $T_m$  elements while assuring full melting of high- $T_m$  elements?
2. How to reduce the oxidation of active elements.
3. How to avoid element segregation in a multi-element system?



元素	熔点/°C
<u>V:</u>	<u>1902</u>
Nb:	2468
Mo:	2610
Ta :	3017
<u>W:</u>	<u>3422</u>

$$\Delta T_m = 1520^\circ\text{C}$$



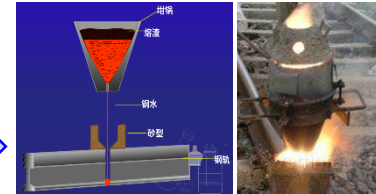
元素	熔点/°C
<u>Cr:</u>	<u>1857</u>
<u>Mn:</u>	<u>1244</u>
Fe:	1538
Co:	1495
Ni:	1453

$$\Delta T_m = 600^\circ\text{C}$$

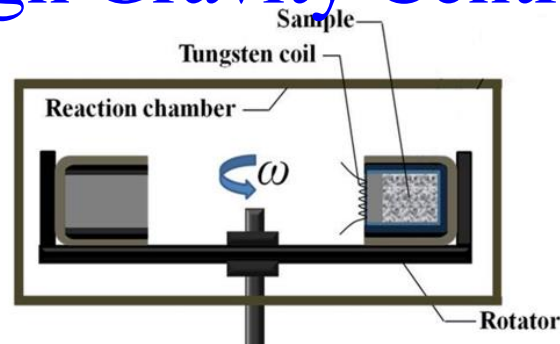
# A new technique to prepare HEA: Combustion Synthesis under High Gravity Progress

Combustion Synthesis  
under High Gravity

Combustion Synthesis



High Gravity Centrifugal



# Many Reaction Systems Available

Reaction system	Product	Melting point	Adiabatic temperature
$\text{Al} + 3/2\text{NiO} \rightarrow 3/2\text{Ni} + 1/2\text{Al}_2\text{O}_3$	Ni	1726	3524
$\text{Al} + 8/3\text{Co}_3\text{O}_4 \rightarrow 9/8\text{Co} + 1/2\text{Al}_2\text{O}_3$	Co	1768	4181
$\text{Al} + 3/2\text{CuO} \rightarrow \text{Cu} + 1/2\text{Al}_2\text{O}_3$	Cu	1357	3000
$\text{Al} + 1/2\text{Cr}_2\text{O}_3 \rightarrow \text{Cr} + 1/2\text{Al}_2\text{O}_3$	Cr	2130	2831
$\text{Al} + 1/2\text{CrO}_3 \rightarrow 1/2\text{Cr} + 1/2\text{Al}_2\text{O}_3$	Cr	2130	4000
$\text{Al} + 3/10\text{V}_2\text{O}_5 \rightarrow 6/10\text{V} + 1/2\text{Al}_2\text{O}_3$	V	2175	3785
$\text{Al} + 1/2\text{WO}_3 \rightarrow 1/2\text{W} + 1/2\text{Al}_2\text{O}_3$	W	3680	4280
$\text{Al} + 1/2\text{Fe}_2\text{O}_3 \rightarrow \text{Fe} + 1/2\text{Al}_2\text{O}_3$	Fe	1809	3622
$14\text{Al} + 3\text{CrO}_3 + 6\text{SiO}_2 \rightarrow 3\text{CrSi}_2 + 7\text{Al}_2\text{O}_3$	CrSi <sub>2</sub>	1748	3600
$14\text{Al} + 3\text{MoO}_3 + 6\text{SiO}_2 \rightarrow 3\text{MoSi}_2 + 7\text{Al}_2\text{O}_3$	MoSi <sub>2</sub>	2293	3200

> 2800K

# Combustion Synthesis under High Gravity

Combustion Synthesis



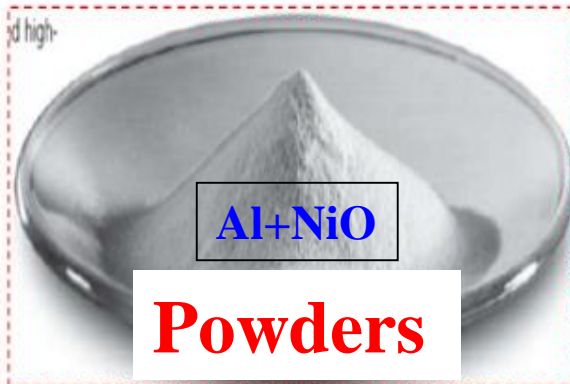
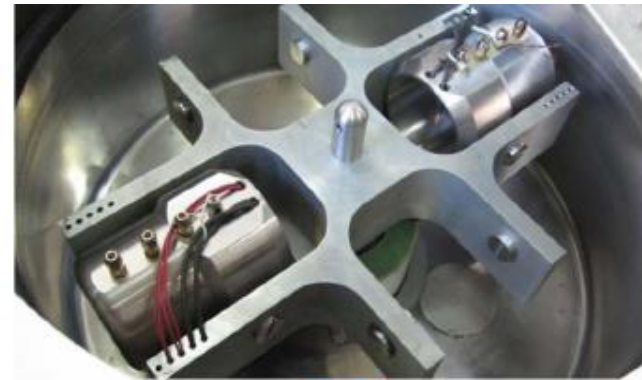
Ultrahigh Temperature  
Reaction, Melting



Centrifugal rotation



High Gravity  
Separate, Solidification



# Outline

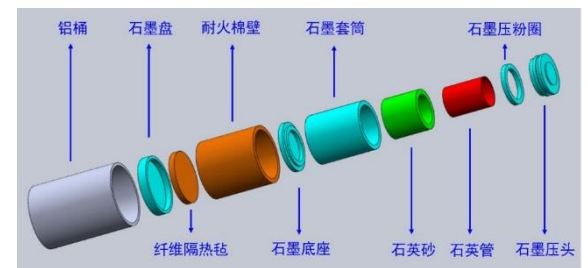
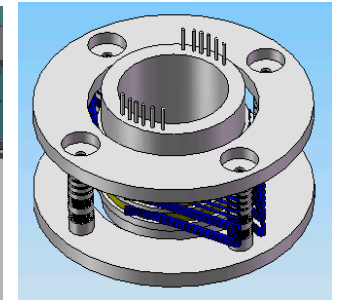
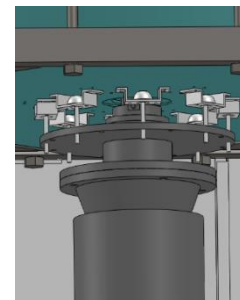
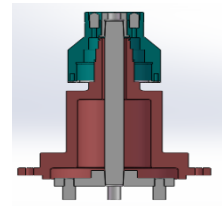
1. Introduction

**2. Experimental**

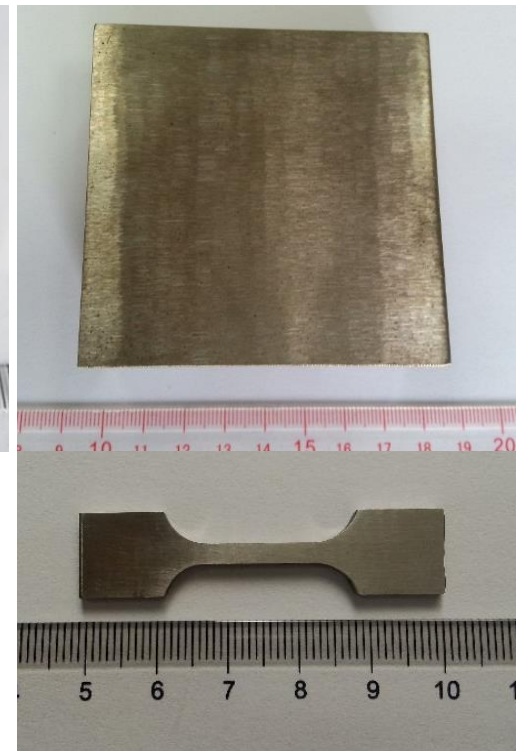
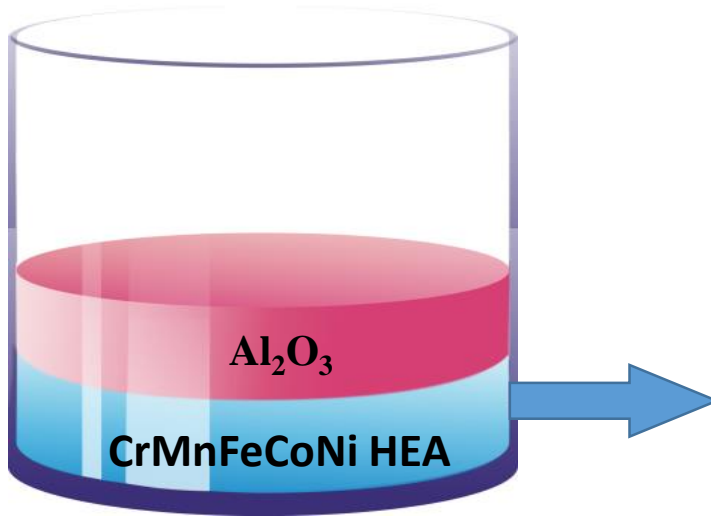
3. Results and discussion

4. Conclusions

# Facilities



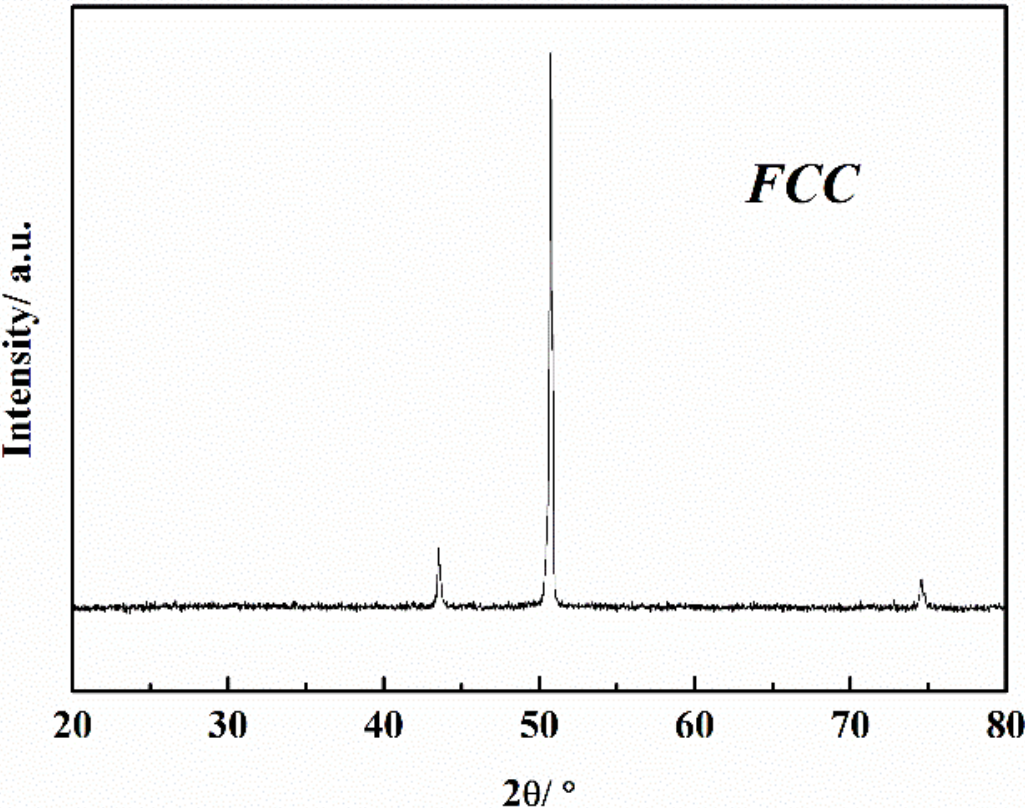
# Preparation of CrMnFeCoNi HEA



# Outline

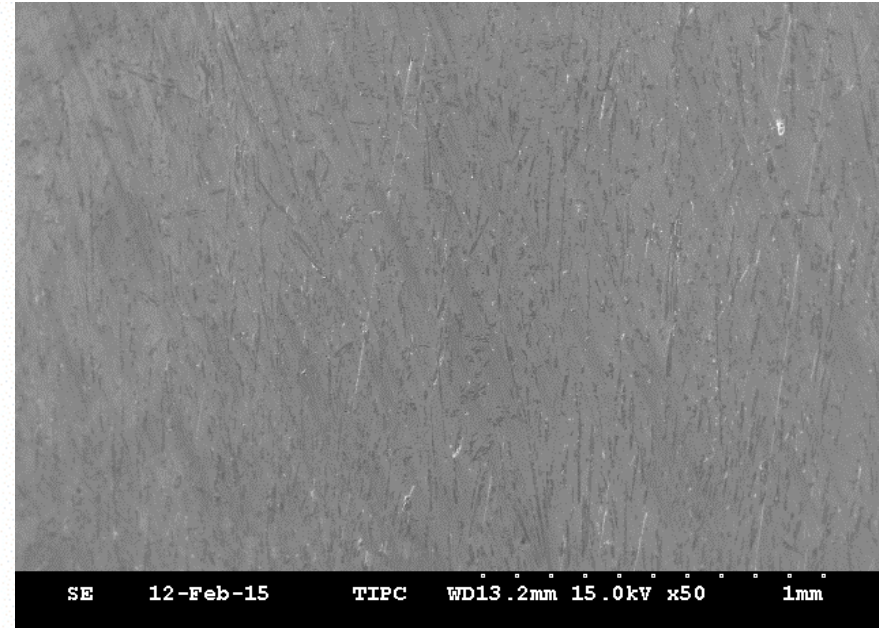
1. Introduction
2. Experimental
- 3. Results and discussion**
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# XRD and SEM/EDS



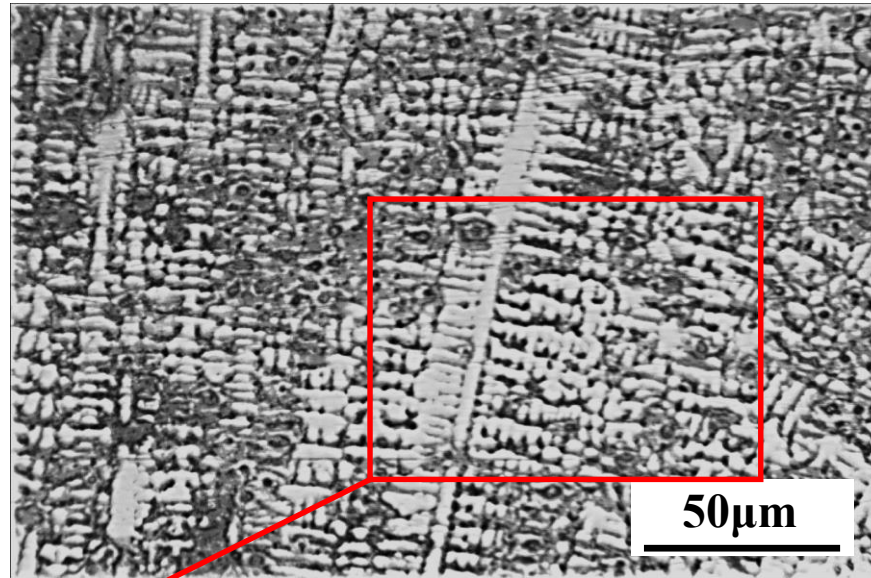
Density: 8.01 g/cm<sup>3</sup>

H<sub>v</sub>: 1.73 GPa

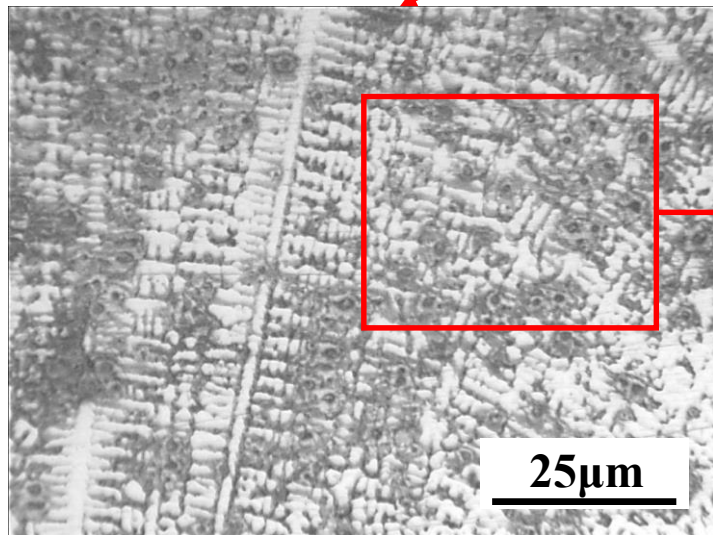


Element	Wt%	Mol%
Cr K	17.15	18.53
Mn K	19.04	19.47
Fe K	20.41	20.54
Co K	21.20	20.21
Ni K	22.20	21.25
Total	100.00	100.0

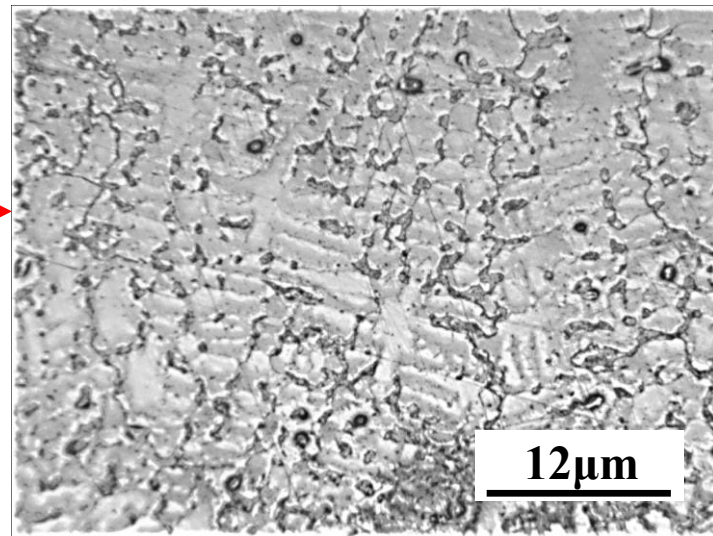
# Optical Micrographs



50×

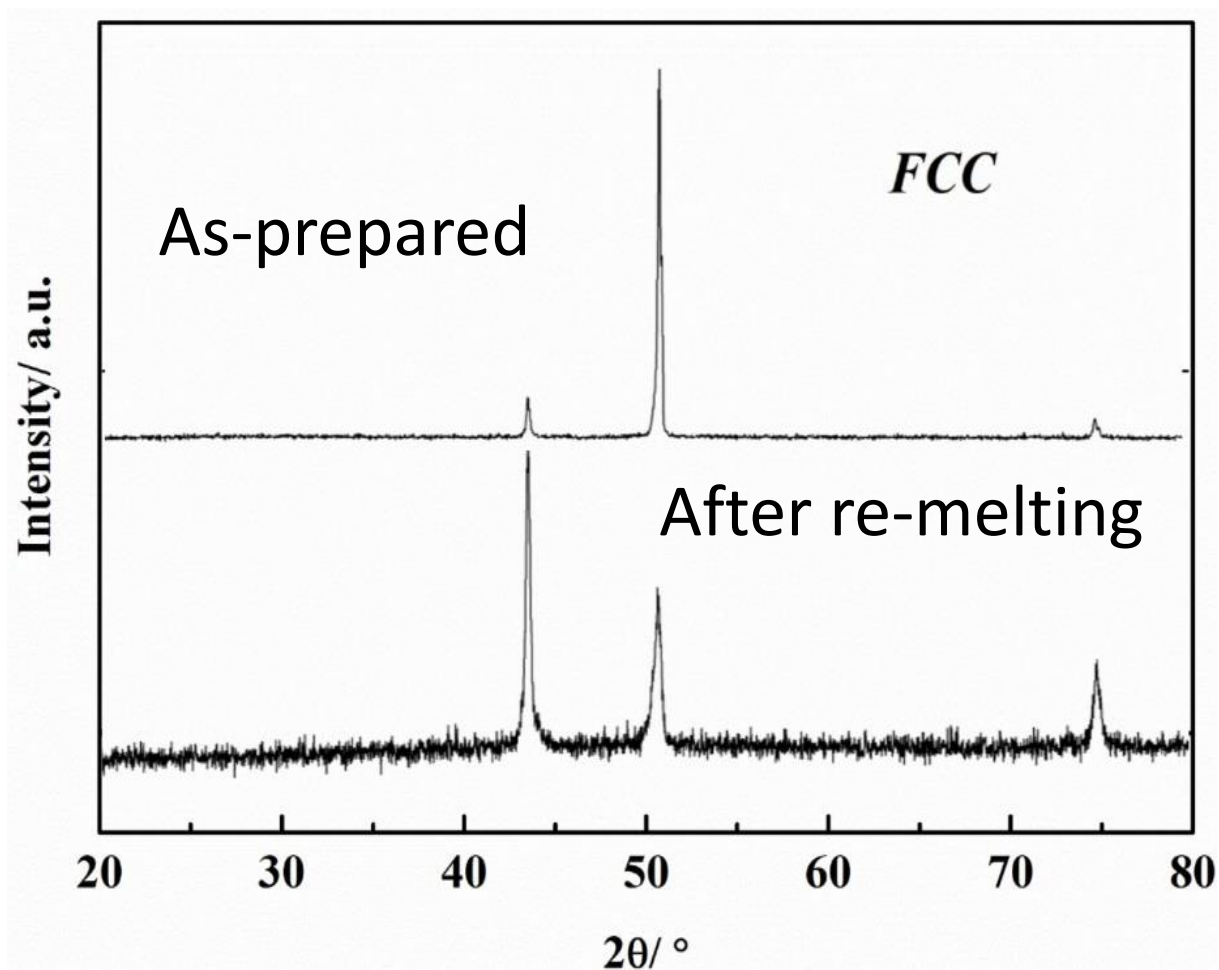


100×

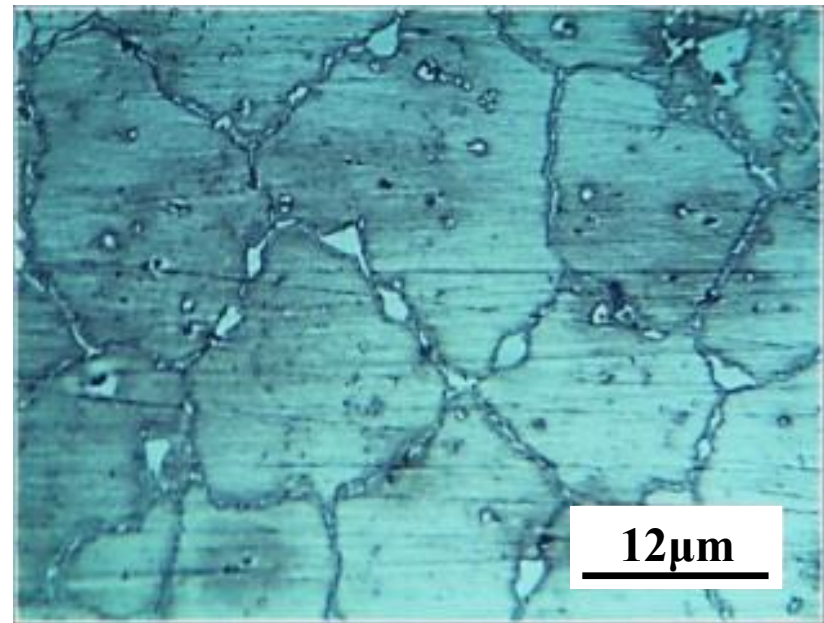
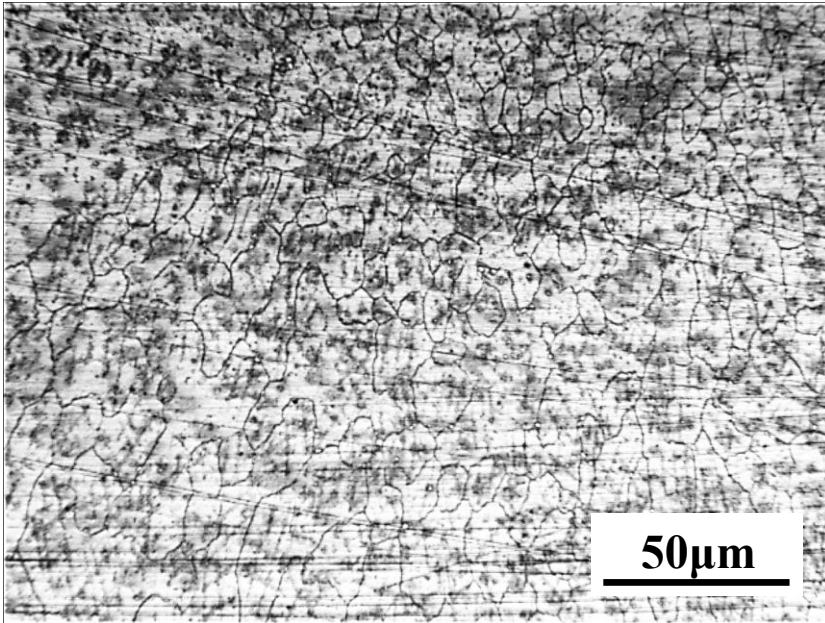


200×

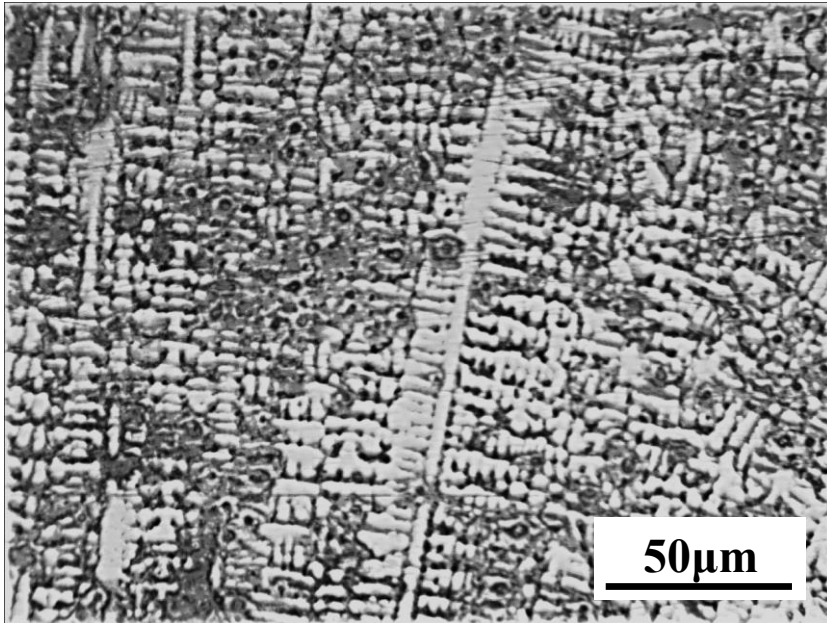
## XRD after re-melting



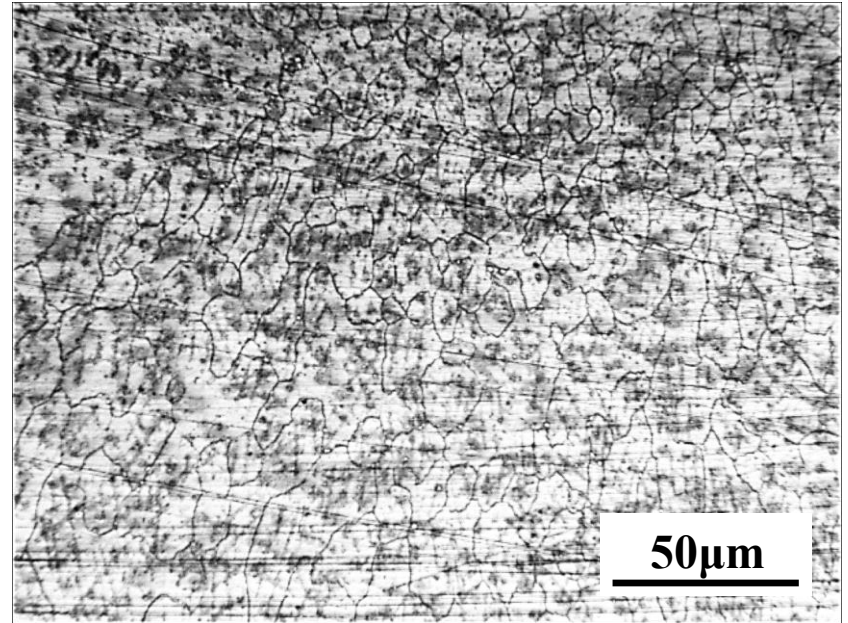
# Optical Micrographs after re-melting



Grain morphology changed after re-melting.



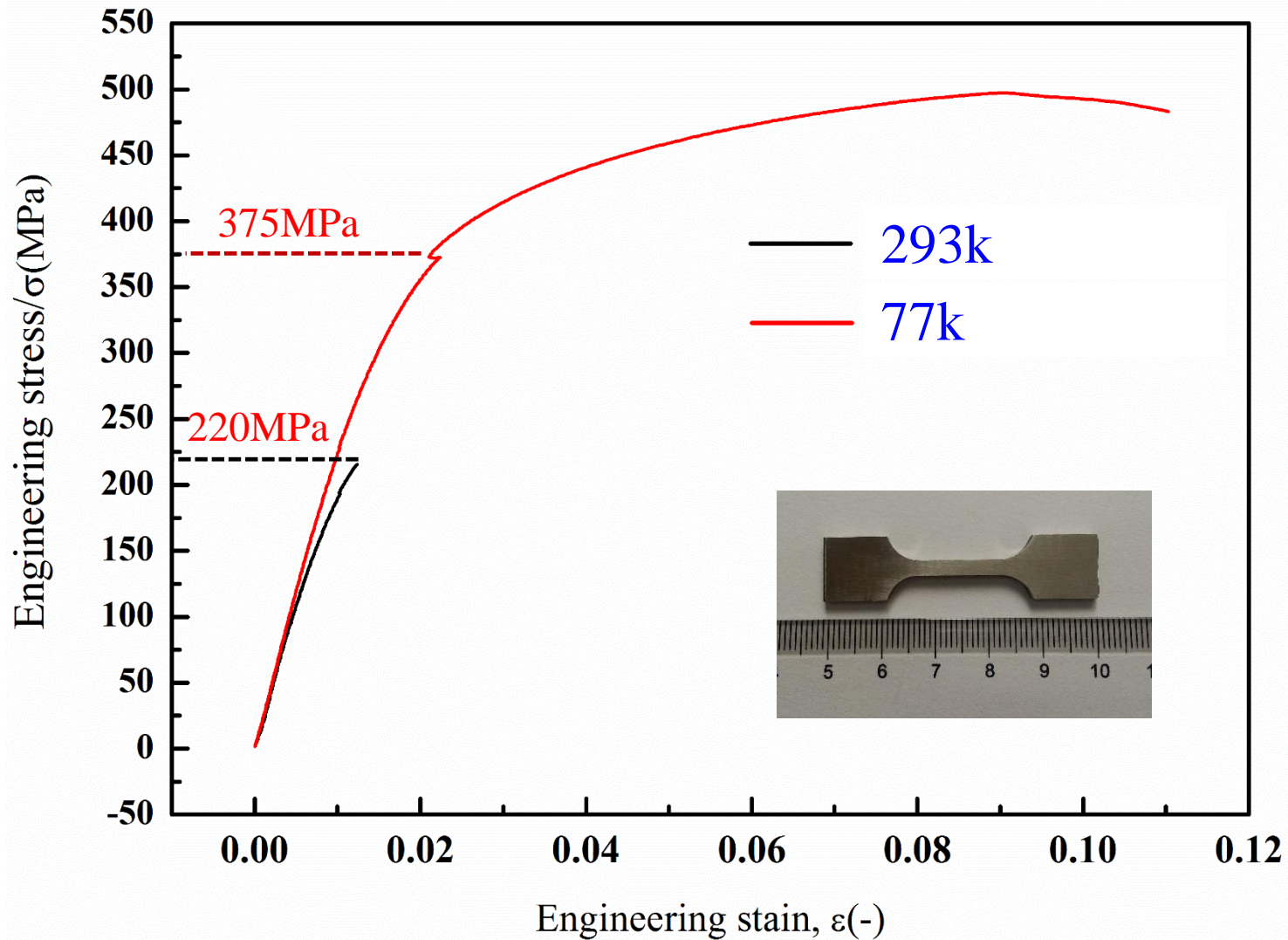
As-prepared



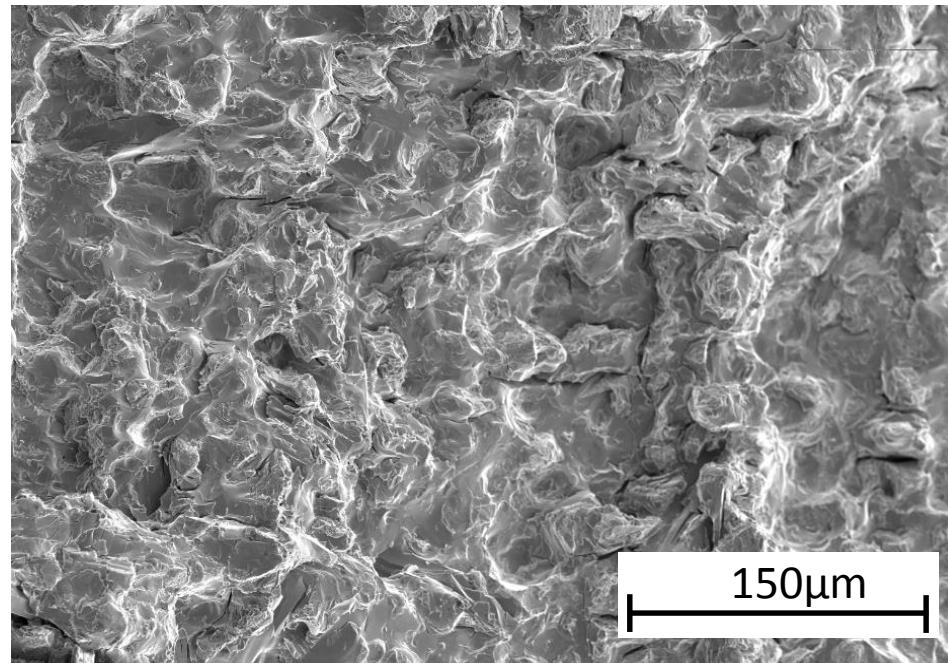
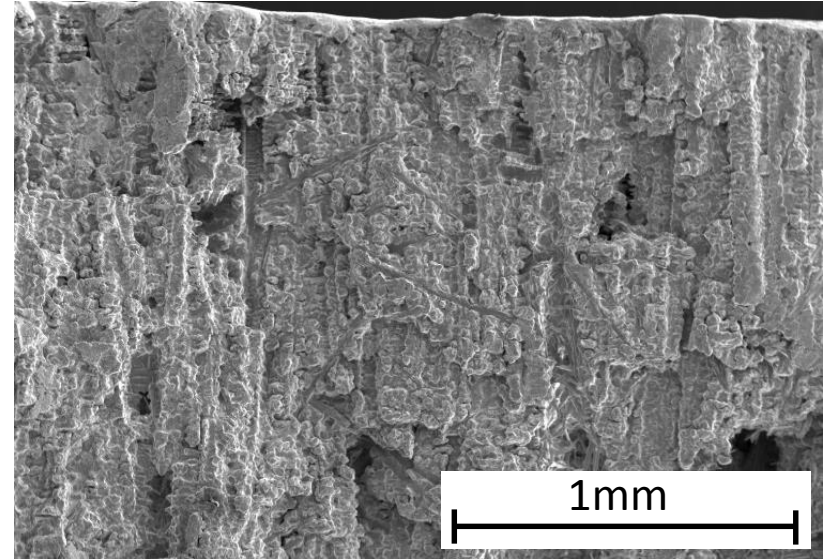
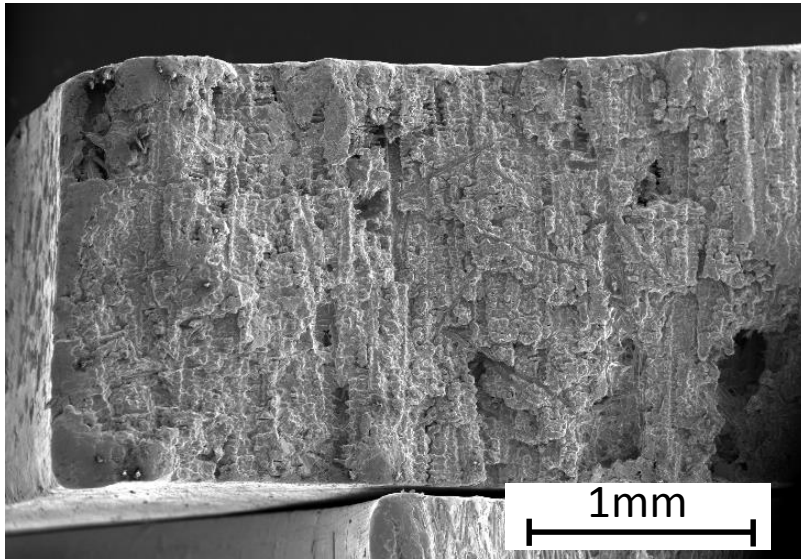
After re-melting

Dendritic → Equiaxed

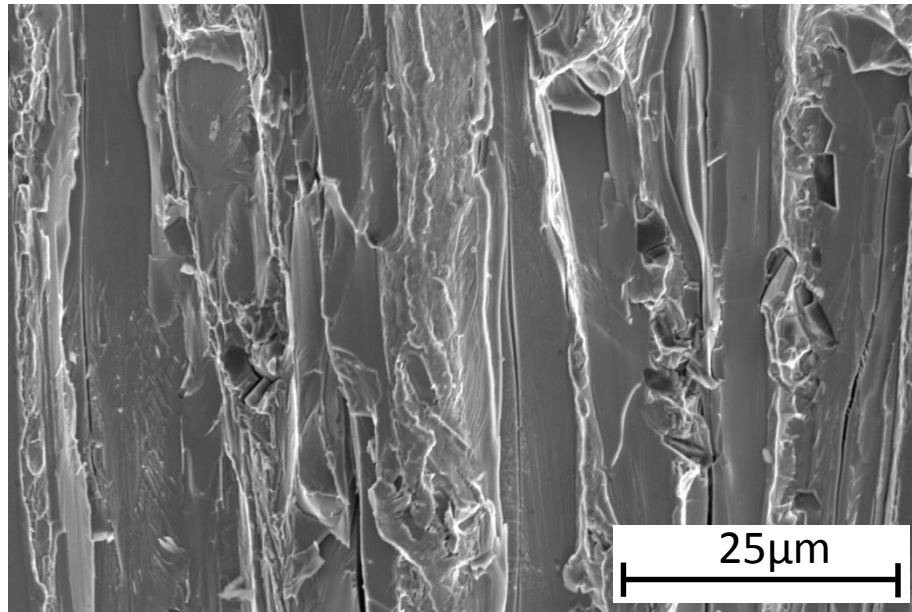
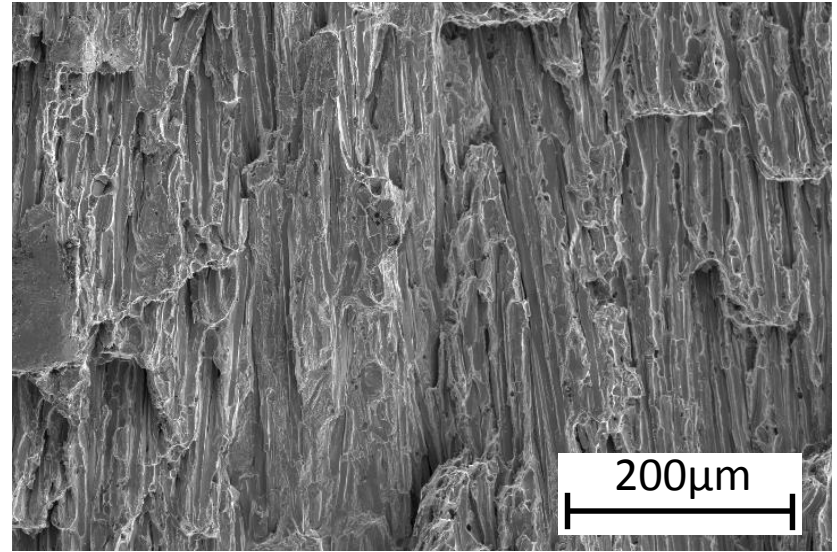
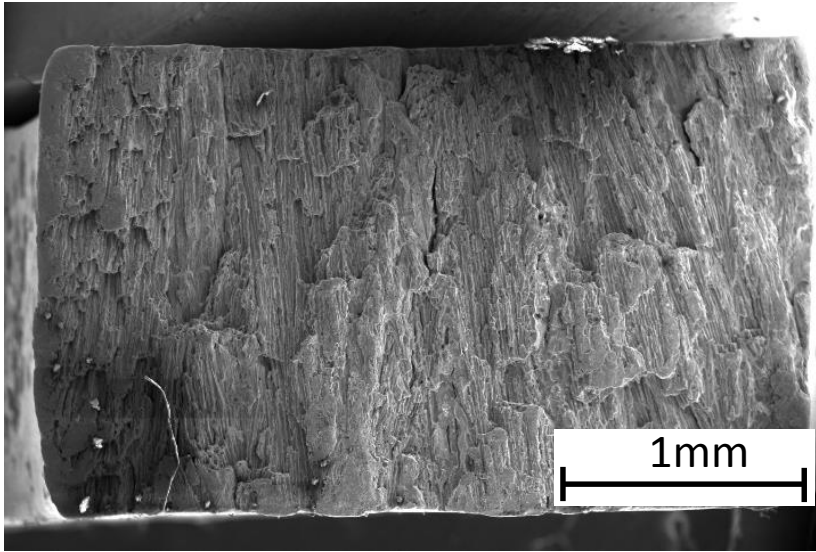
# Tensile test of CrMnFeCoNi HEA



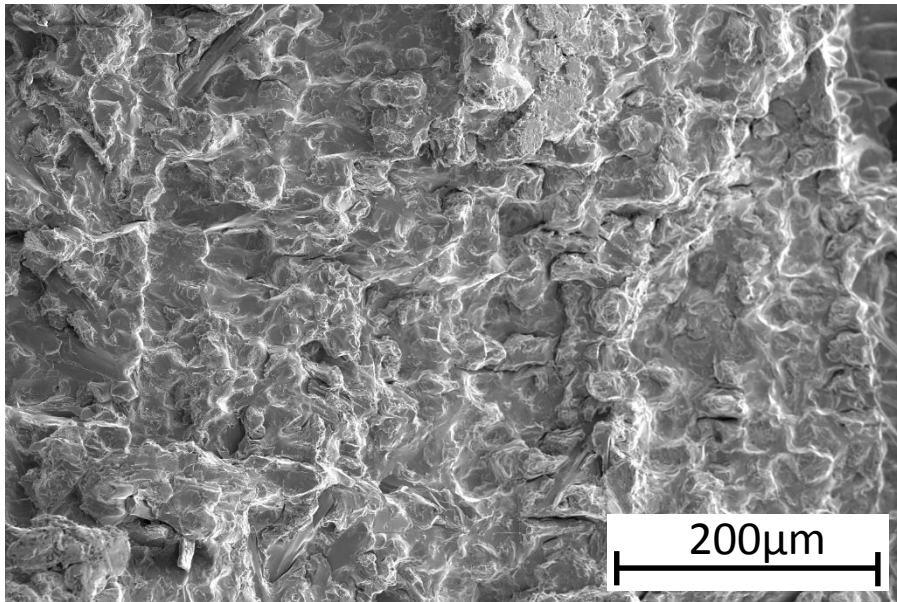
# Morphology of fracture surface (fractured at 293K)



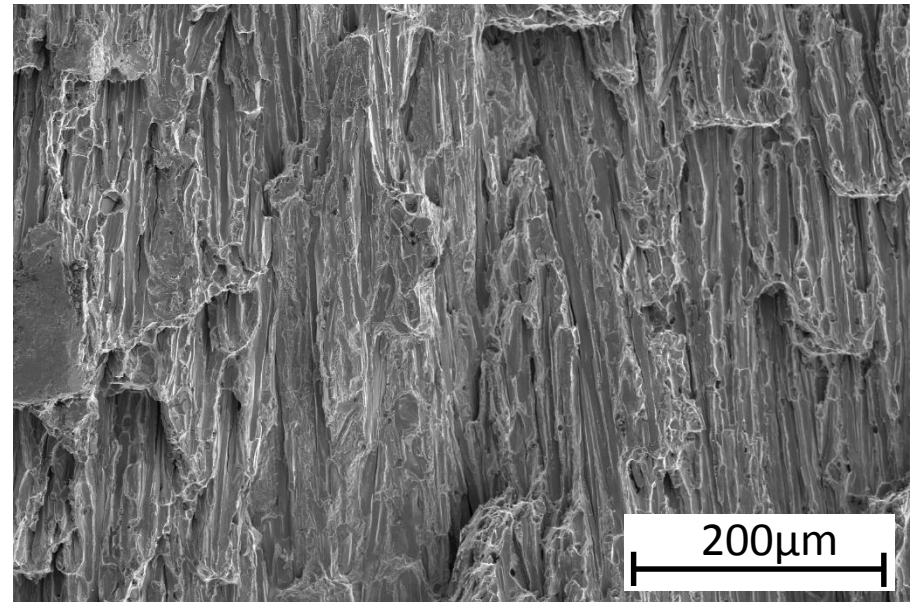
# Morphology of fracture surface (fractured at 77K)



# Comparison of morphology of fracture surface fractured at 293 K and 77 K



**293 K**



**77 K**

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# Conclusions

1. CrMnFeCoNi HEA was successfully prepared by combustion synthesis under high gravity, and showed single FCC lattice structure and dendritic grain morphology.
2. After re-melting, the CrMnFeCoNi HEA still kept the FCC structure, but the grain morphology became equiaxed.
3. The CrMnFeCoNi HEA exhibited brittle fracture at room temperature, but showed ductile behavior at 77 K, with much-improved strength and strain.

**From the experiment results, combustion synthesis under high gravity may offer an alternative and more efficient way for preparing HEAs with promising cryogenic properties.**