EPNM-2016

Combustion synthesis of high-entropy alloys and thermoelectric materials

Jiangtao Li

Technical Institute of Physics and Chemistry
Chinese Academy of Sciences

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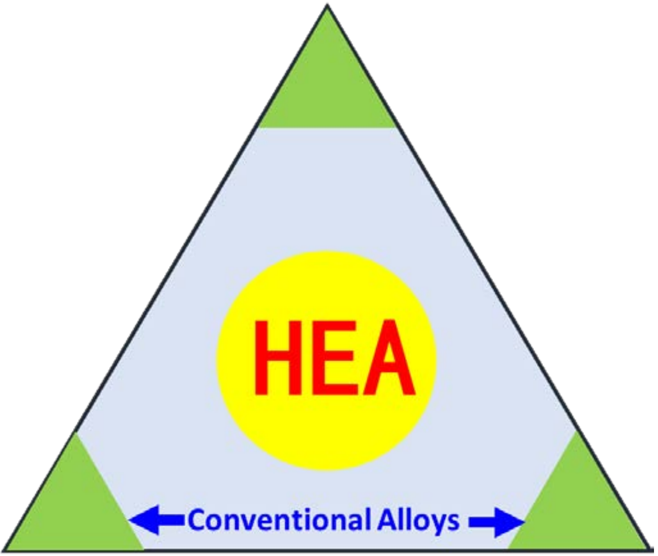
high-entropy alloys

Outline

1. **Introduction**
2. Experimental
3. Results and discussion
4. Conclusions

High Entroy Alloys (HEA)



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

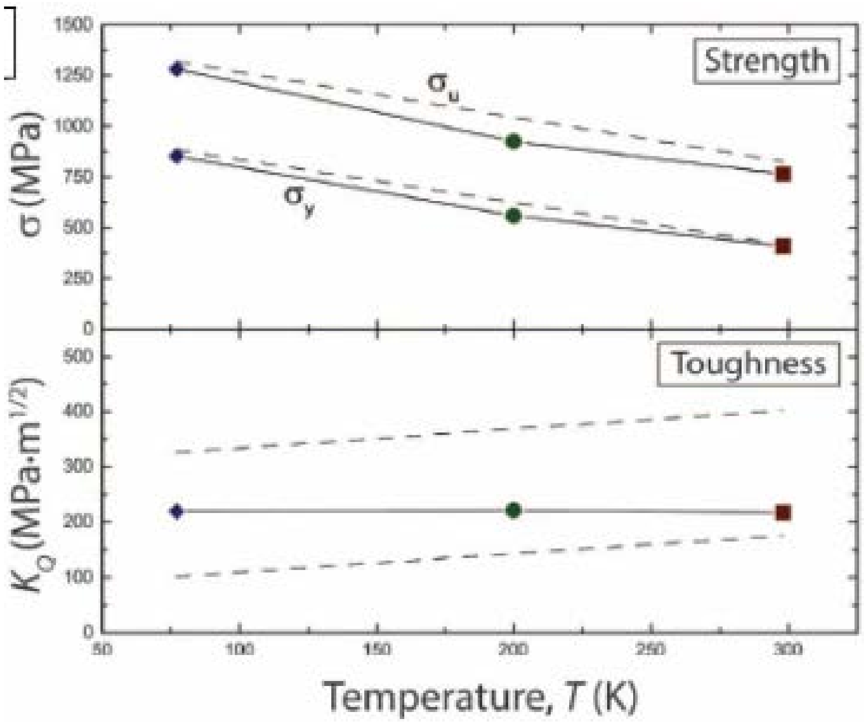
$$G = H\text{-}TS,\ \ S\uparrow \rightarrow G\downarrow$$

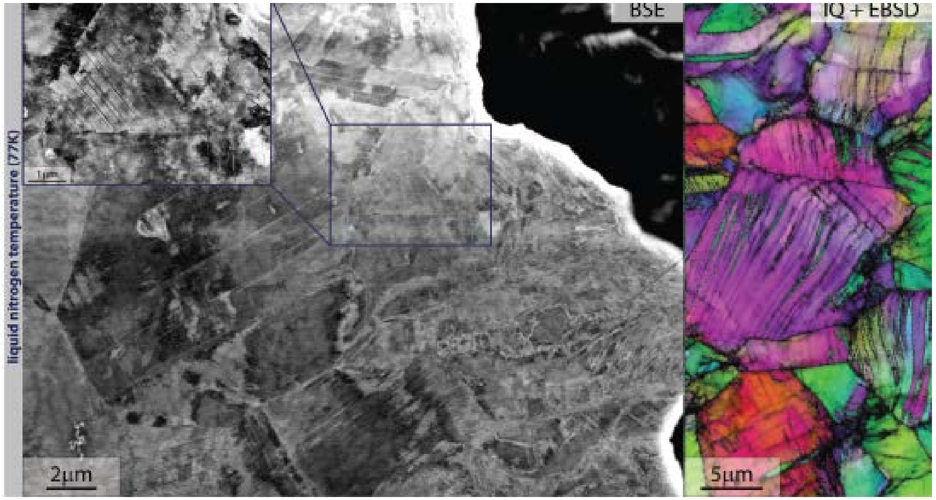
The configurational entropy contribution to the total free energy in alloys with five or more major elements may stabilize the solid-solution state relative to multiphase microstructures.

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

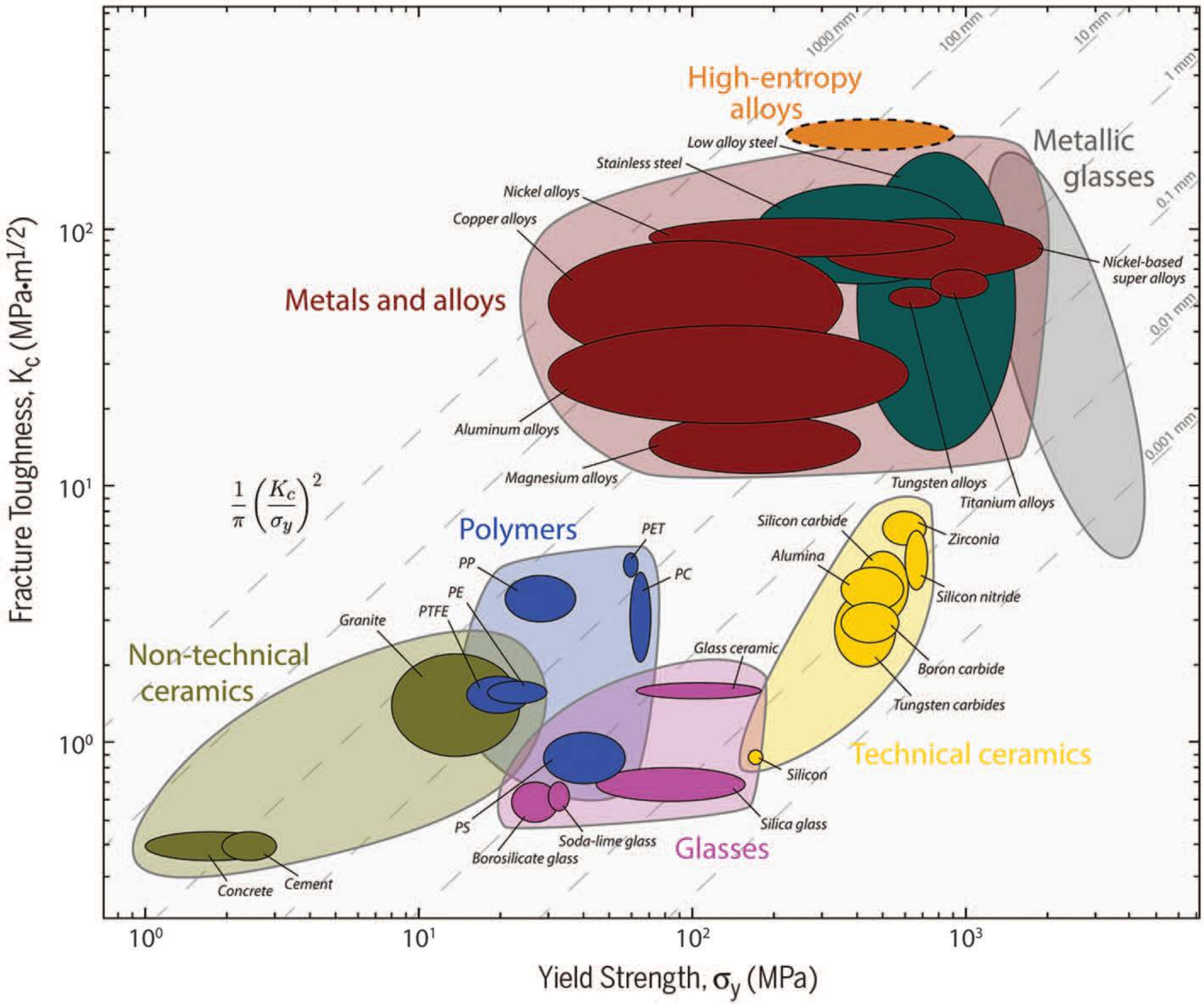
CrMnFeCoNi HEA: Improved properties at Low T

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)



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

Preparation of HEA

Arc melting

Induction melting

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

Much time and energy consumption → 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?

$W_{20}Nb_{20}Ta_{20}Mo_{20}V_{20}$

元素	熔点/℃
V:	**1902**
Nb:	2468
Mo:	2610
Ta :	3017
W:	3422

ΔT_m=1520℃

CrMnFeCoNi

元素	熔点/℃
Cr:	**1857**
Mn:	1244
Fe:	1538
Co:	1495
Ni:	1453

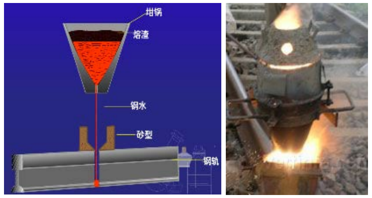
ΔT_m=600℃

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

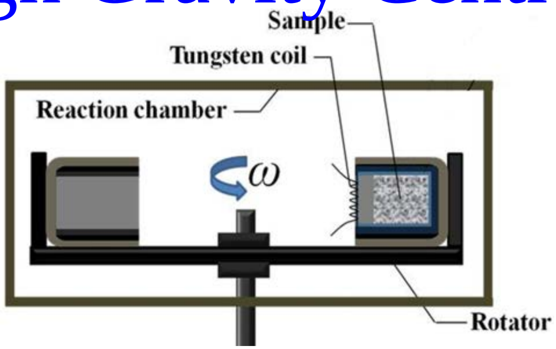
Combustion Synthesis under High Gravity =

Combution Synthesis

$Al+Fe_2O_3 \rightarrow Al_2O_3+Fe$



High Gravity Centrifugal



Many Reaction Systems Available

Reaction system	Product	Melting point	Adiabatic temperature
$Al+3/2NiO \rightarrow 3/2Ni+1/2Al_2O_3$	Ni	1726	3524
$Al+8/3Co_3O_4 \rightarrow 9/8Co+1/2Al_2O_3$	Co	1768	4181
$Al+3/2CuO \rightarrow Cu+1/2Al_2O_3$	Cu	1357	3000
$Al+1/2Cr_2O_3 \rightarrow Cr+1/2Al_2O_3$	Cr	2130	2831
$Al+1/2CrO_3 \rightarrow 1/2Cr+1/2Al_2O_3$	Cr	2130	4000
$Al+3/10V_2O_5 \rightarrow 6/10V+1/2Al_2O_3$	V	2175	3785
$Al+1/2WO_3 \rightarrow 1/2W+1/2Al_2O_3$	W	3680	4280
$Al+1/2Fe_2O_3 \rightarrow Fe+1/2Al_2O_3$	Fe	1809	3622
$14Al+3CrO_3+6SiO_2 \rightarrow 3CrSi_2+7Al_2O_3$	$CrSi_2$	1748	3600
$14Al+3MoO_3+6SiO_2 \rightarrow 3MoSi_2+7Al_2O_3$	$MoSi_2$	2293	3200

>2800K

Combustion Synthesis under High Gravity

Combustion Synthesis

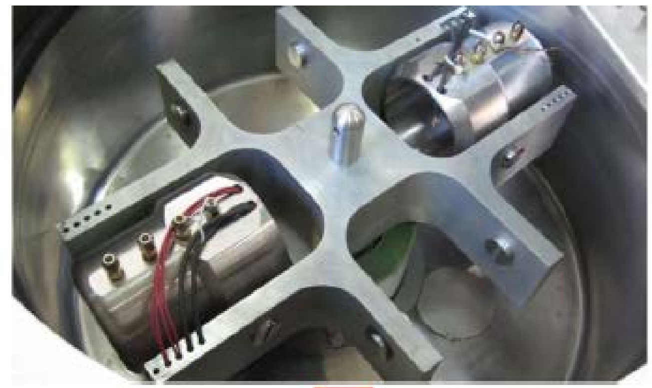
Ultrahigh Temperature

Reaction、Melting

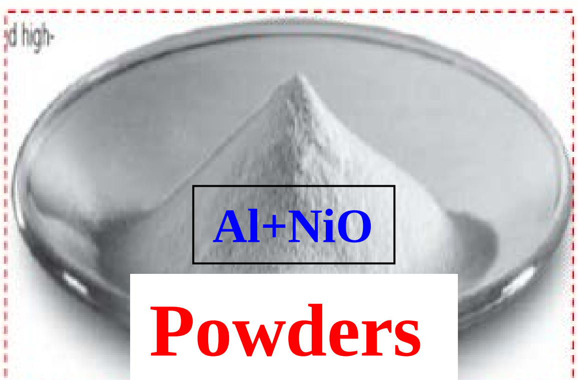
Centrifugal rotation

High Gravity

Separate、Solidification



$$\mathbf{Al + 3/2NiO \xrightarrow{Ignite} 1/2Al_2O_3 + 3/2Ni}$$



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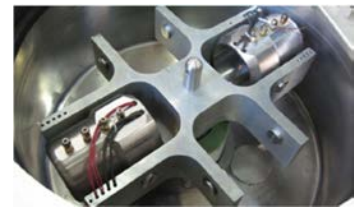
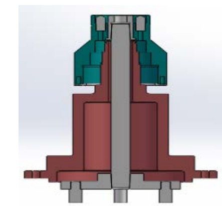
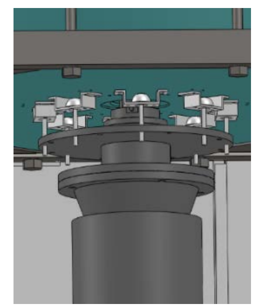
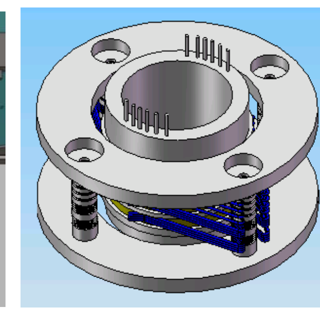
Facilities

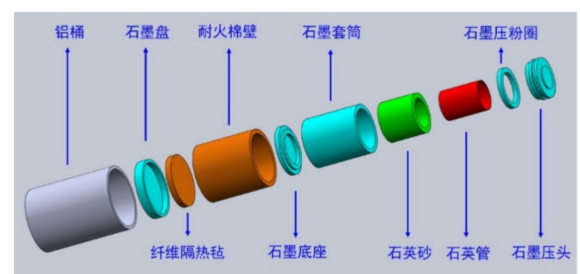

ANBISHENG
CR 50





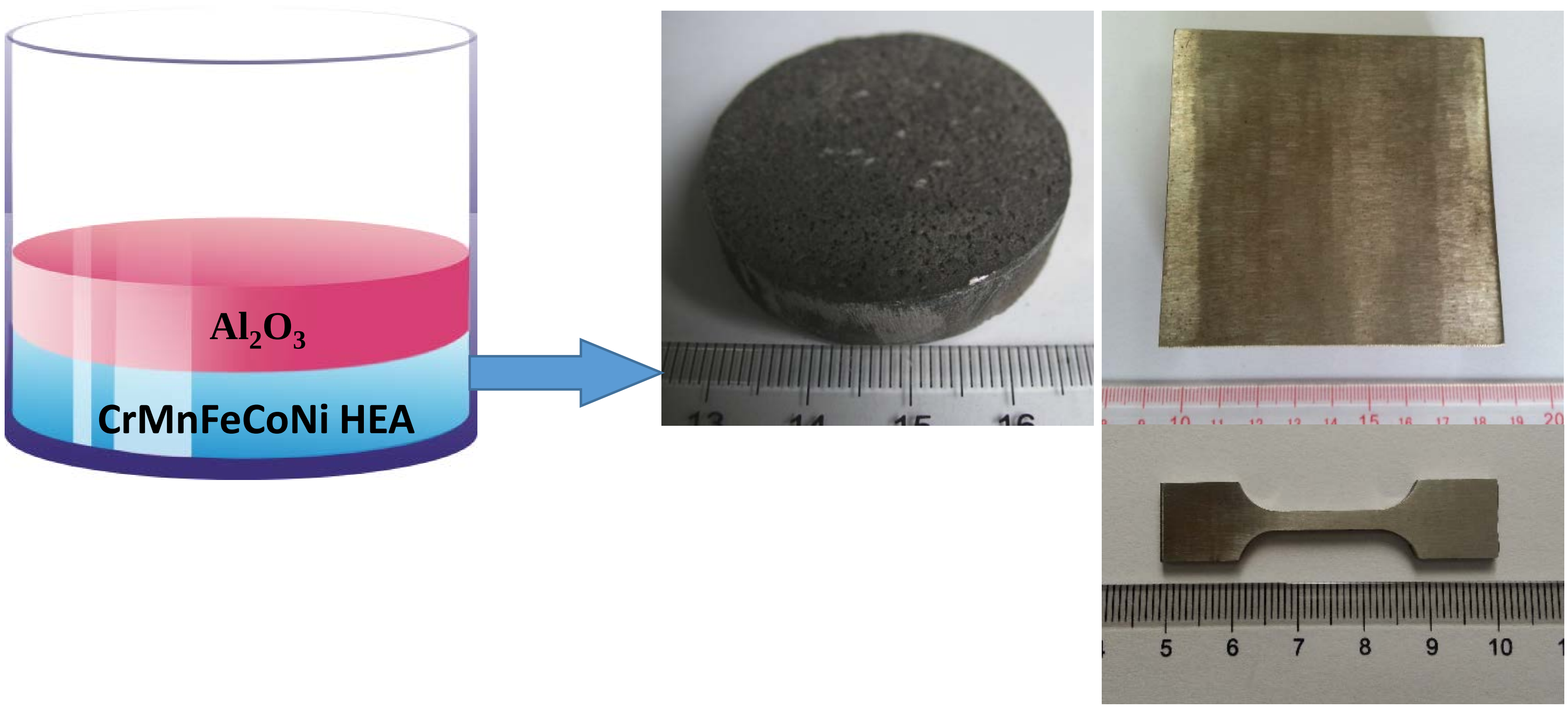





铝桶
石墨盘
耐火棉壁
石墨套筒
石墨压粉圈
纤维隔热毡
石墨底座
石英砂
石英管
石墨压头

Preparation of CrMnFeCoNi HEA

$$Al + Cr_2O_3 + Fe_2O_3 + Co_2O_3 + NiO + Mn \rightarrow Al_2O_3 + \underline{\mathbf{CrMnFeCoNi}}$$



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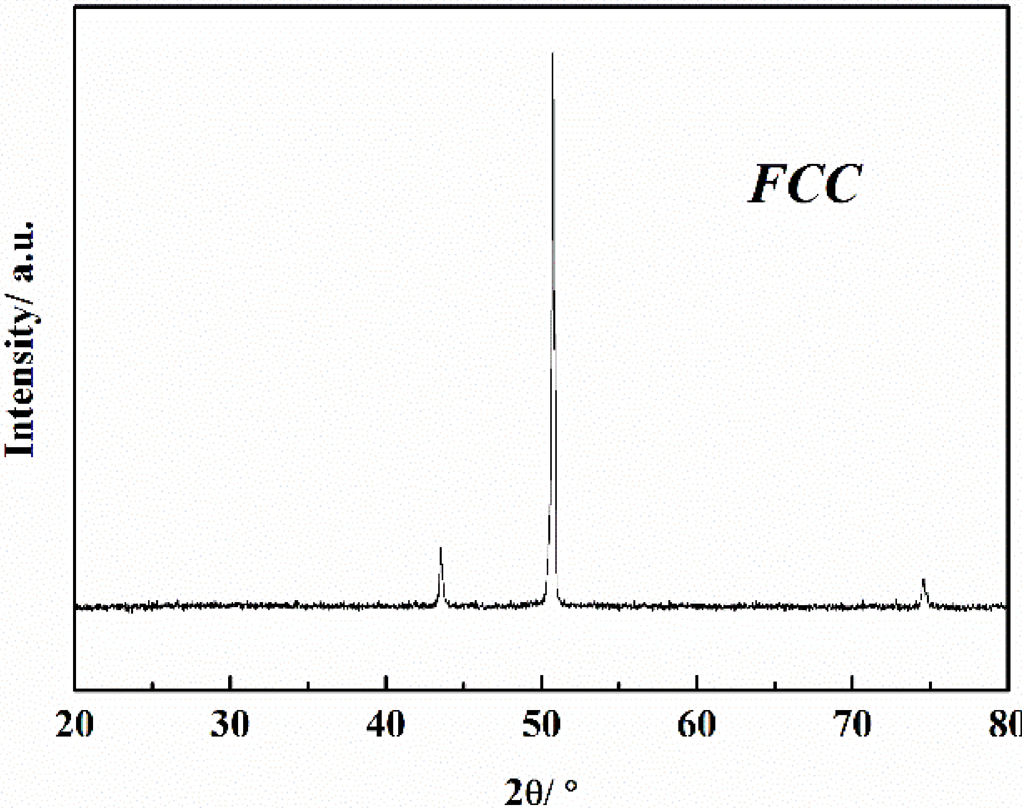
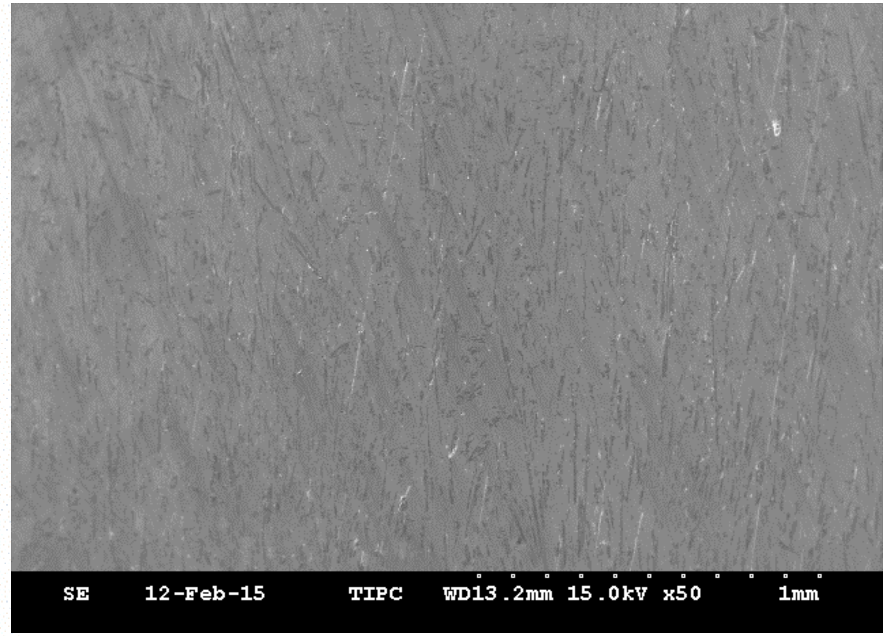
XRD and SEM/EDS



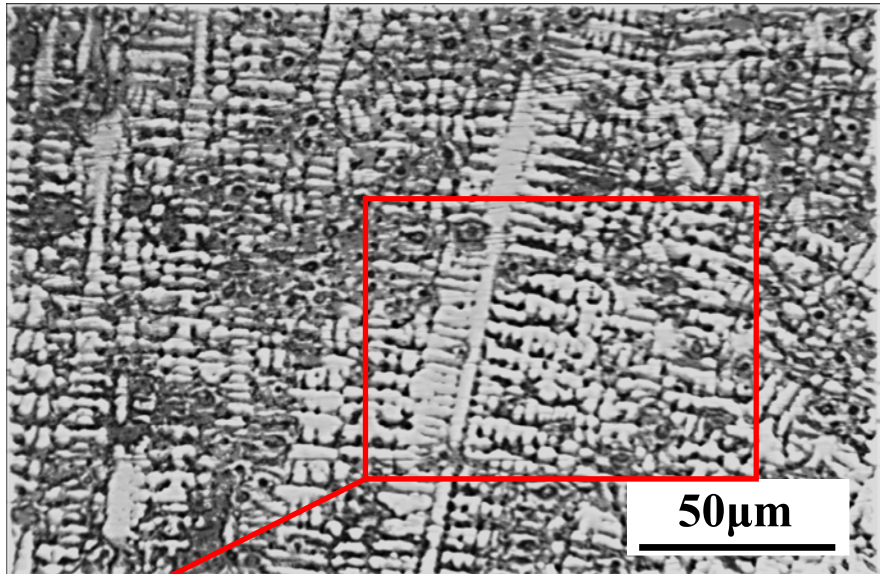


Element	Wt%	Mol%
Cr K	17.15	18.53
Mn K	19.04	19.47
Fe K	20.41	20.54
Co K	21.20	20.21
Ni K	22.20	21.25
Total	100.00	100.0

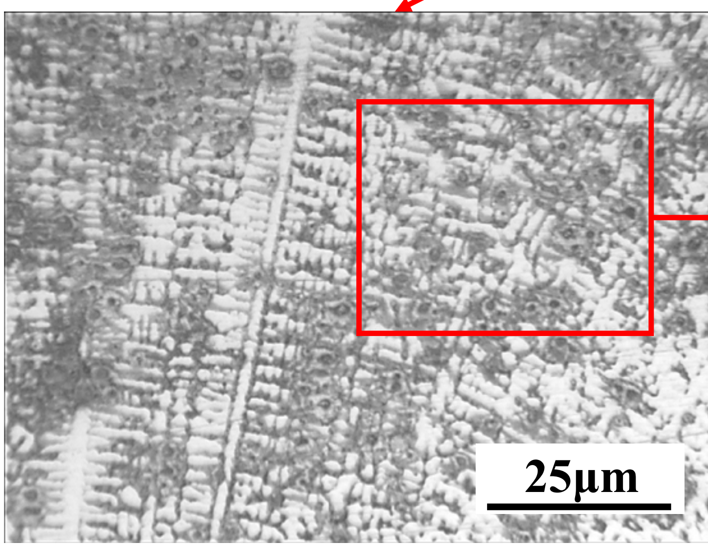
Density: 8.01 g/cm^3

H_V: 1.73 GPa

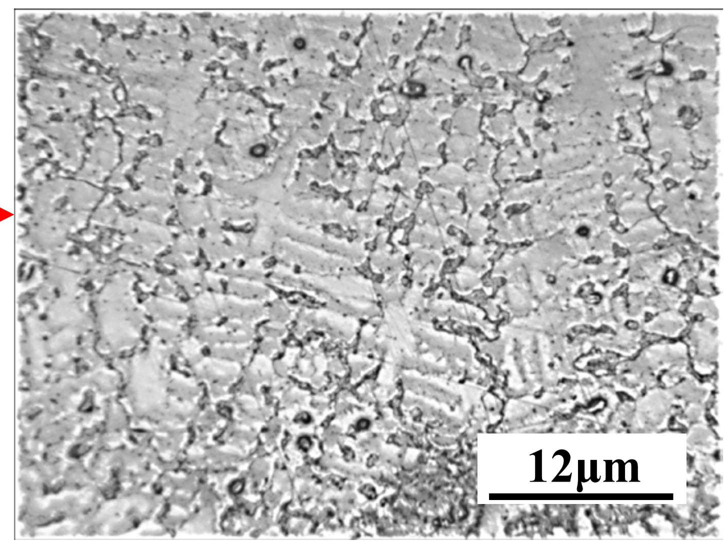
Optical Micrographs



50×

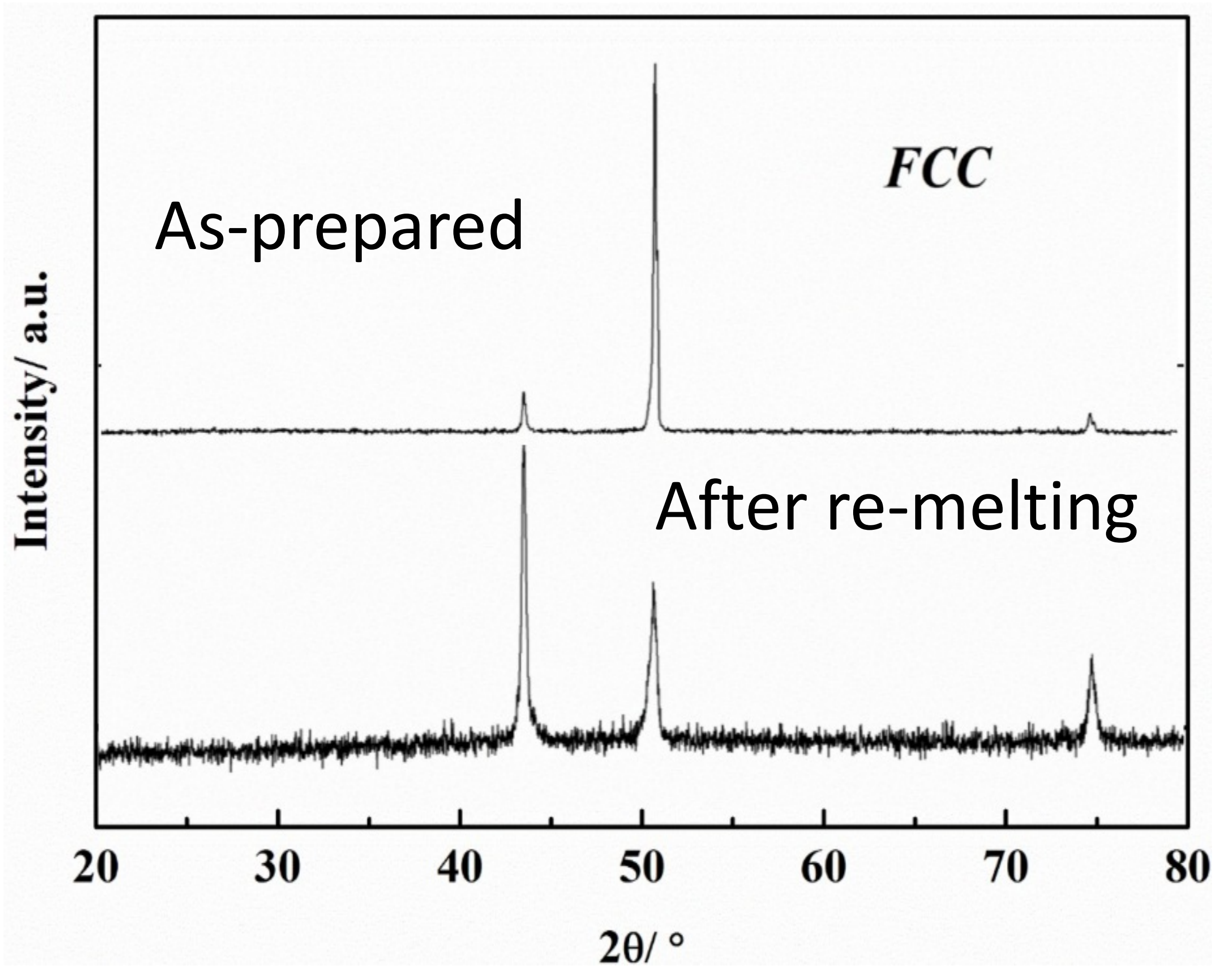


100×

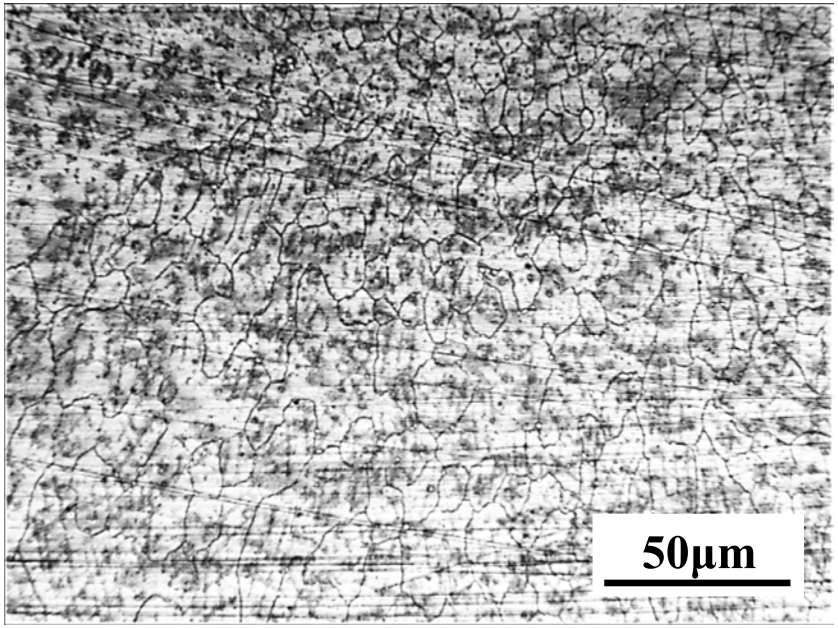


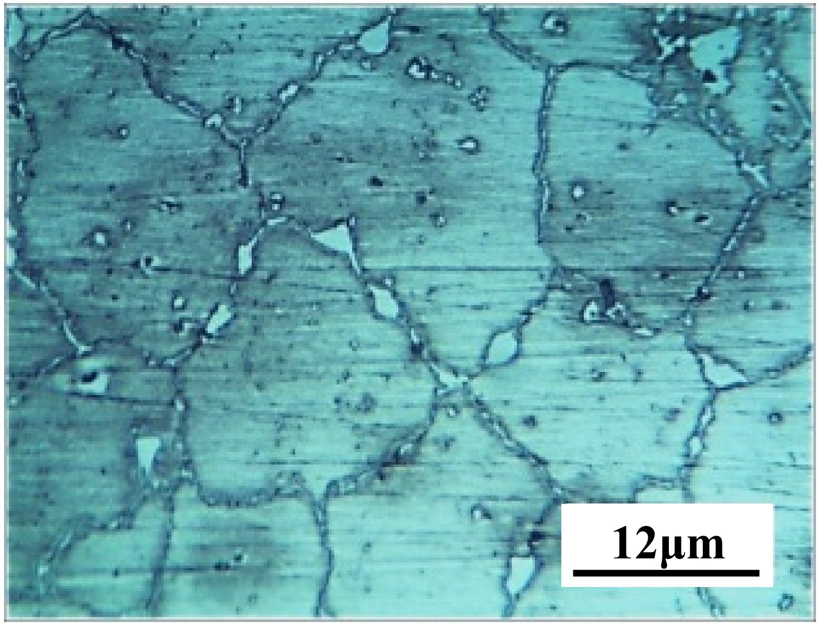
200×

XRD after re-melting

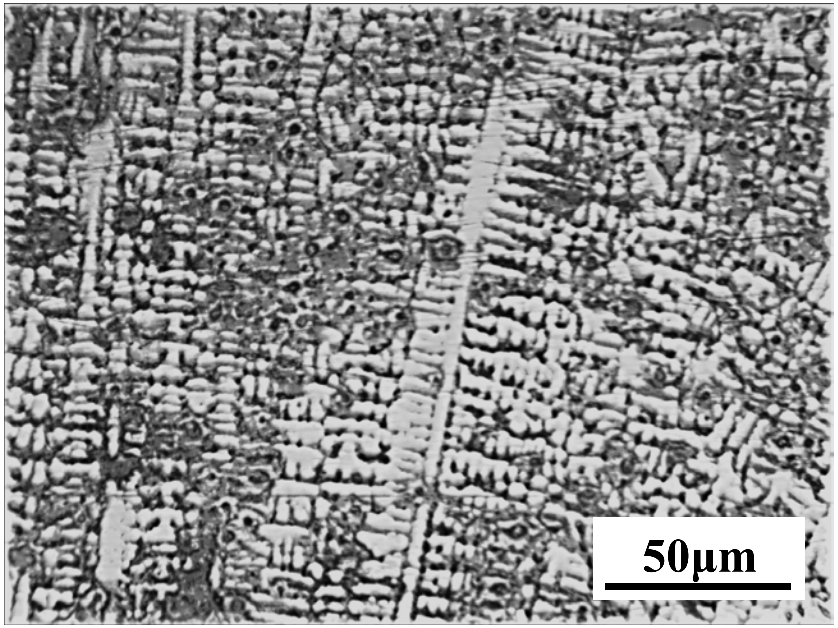


Optical Micrographs after re-melting

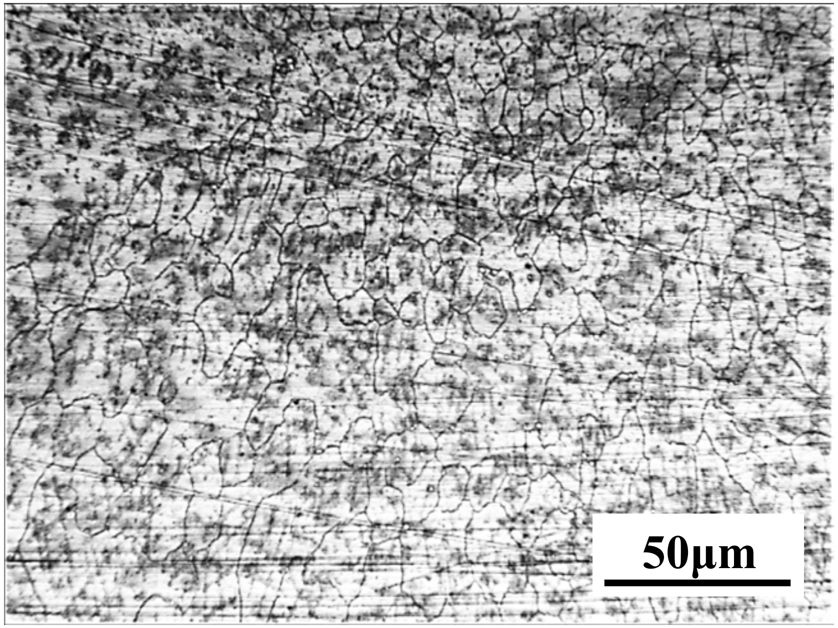




Grain morphology changed after re-melting.



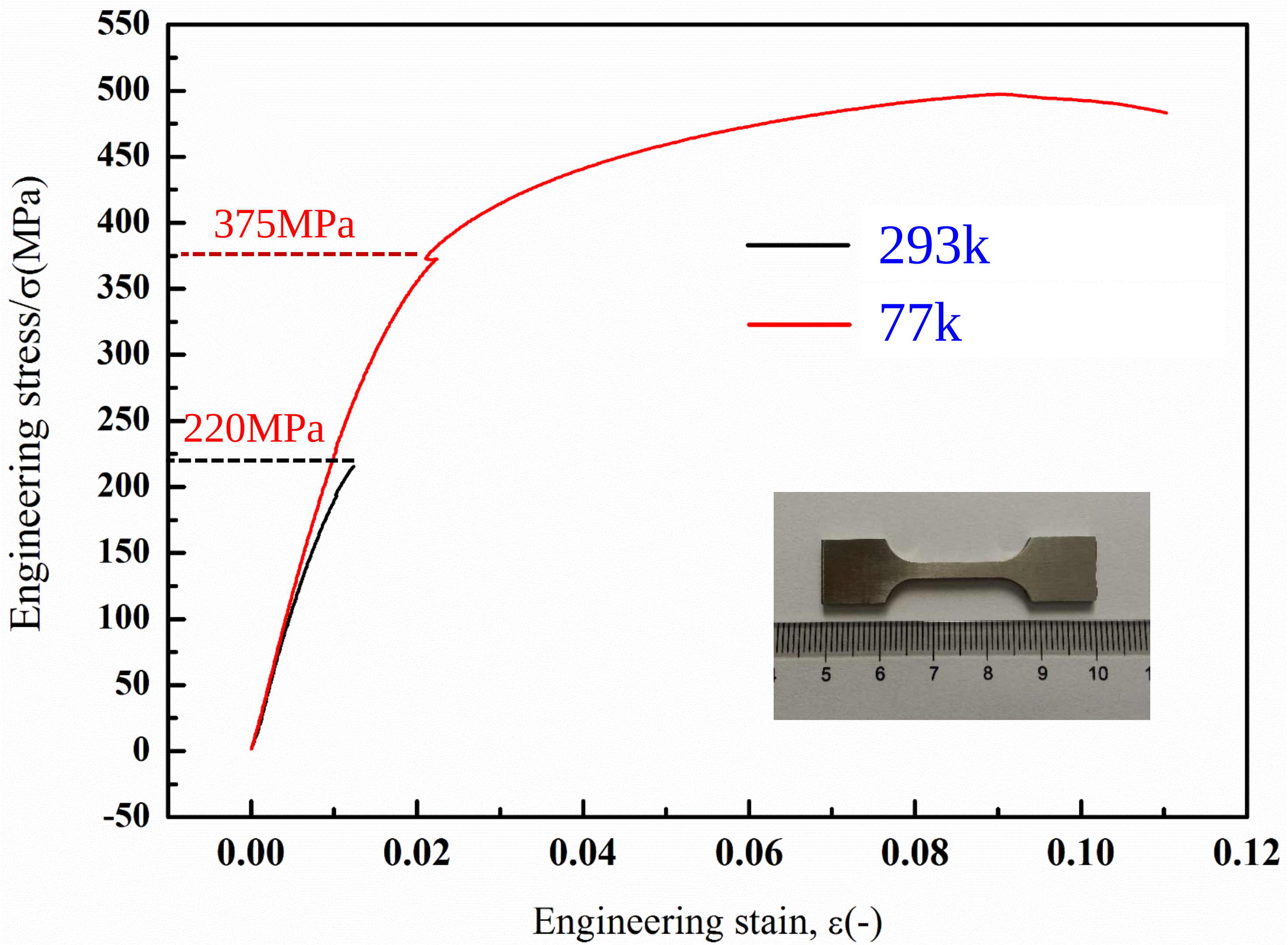
As-prepared



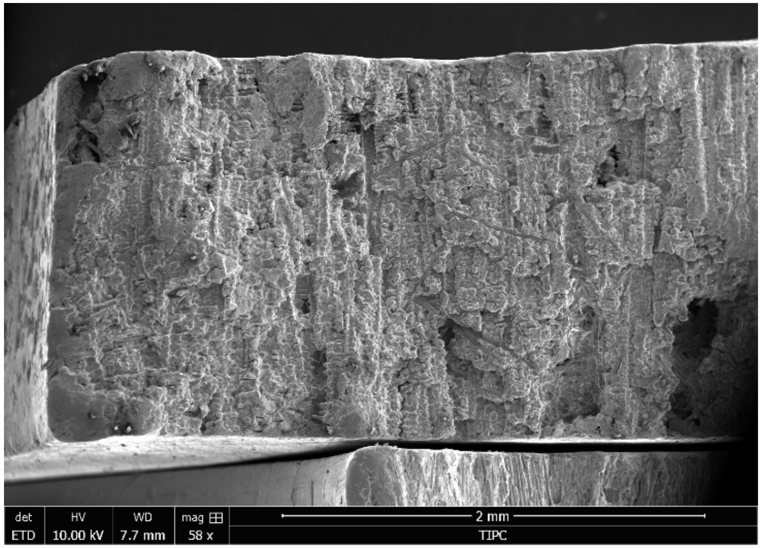
After re-melting

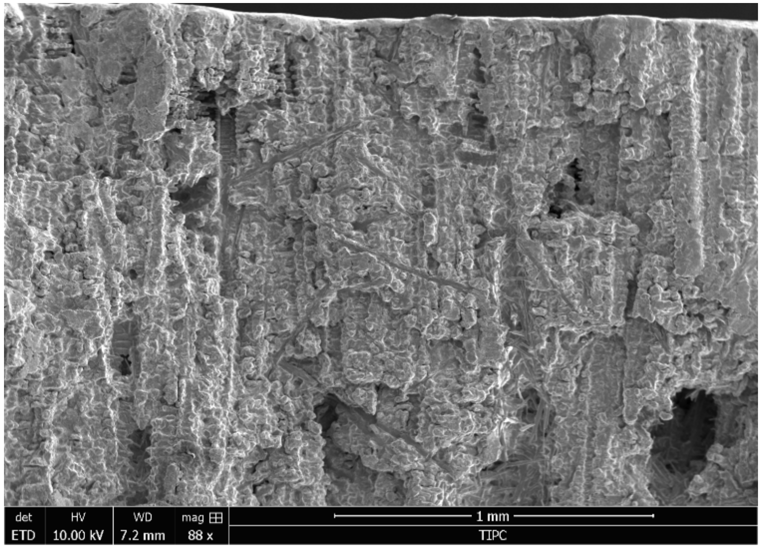
Dentritic → Equiaxed

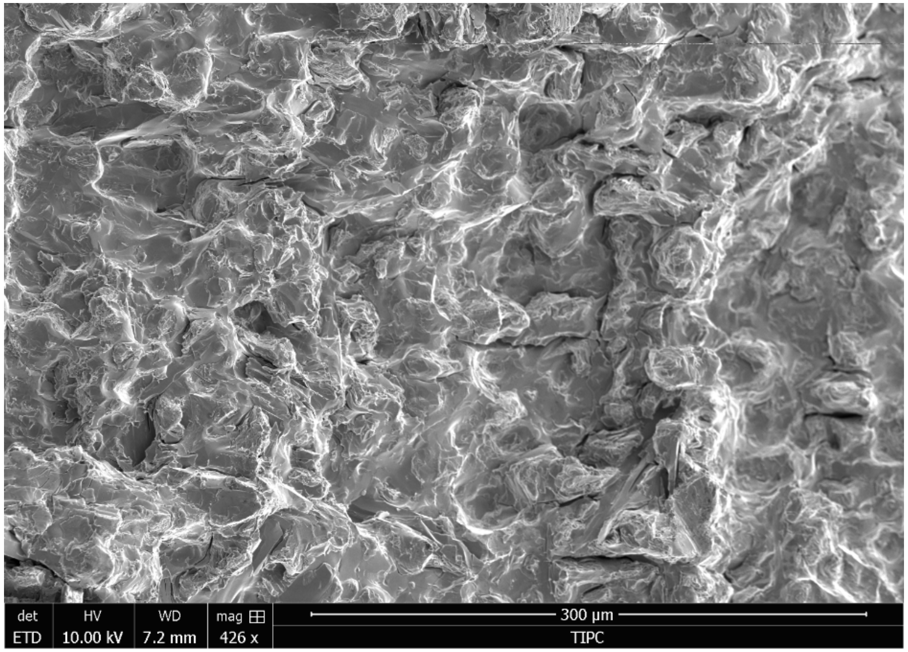
Tensile test of CrMnFeCoNi HEA



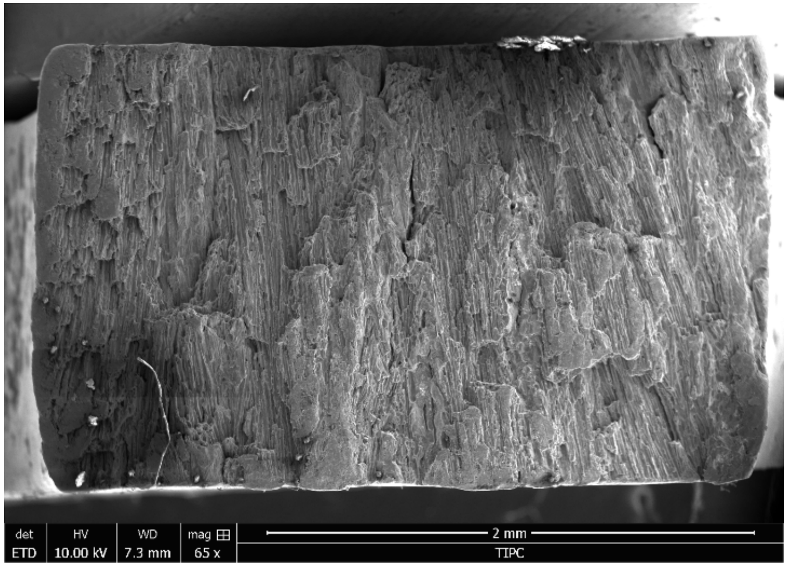
Morphology of fracture surface (fractured at 293K)

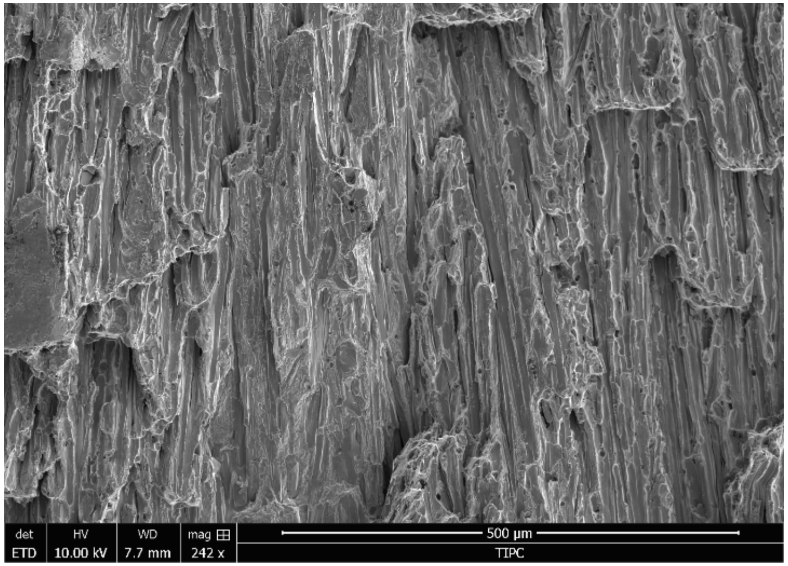


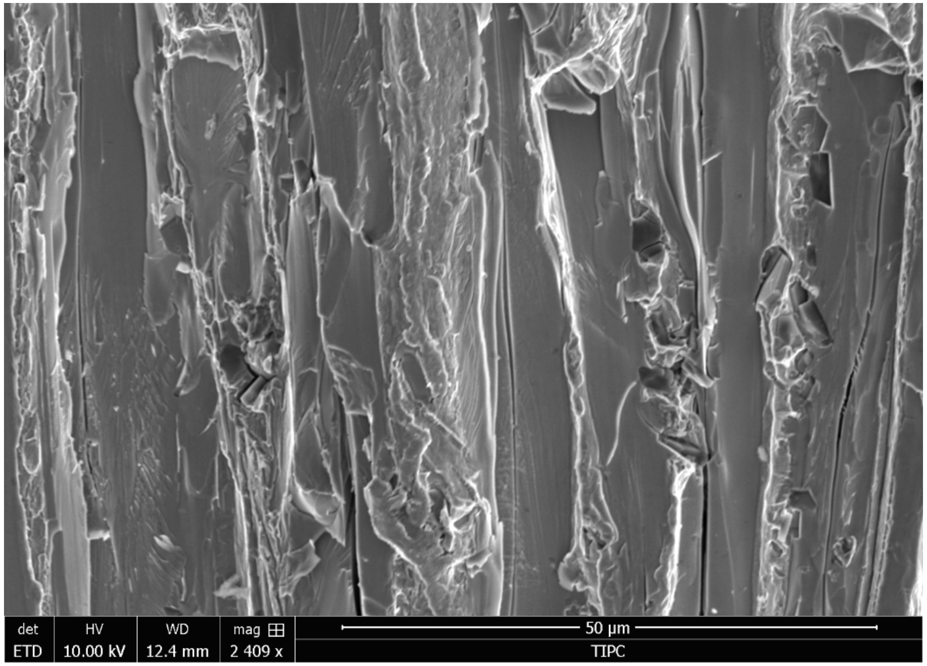




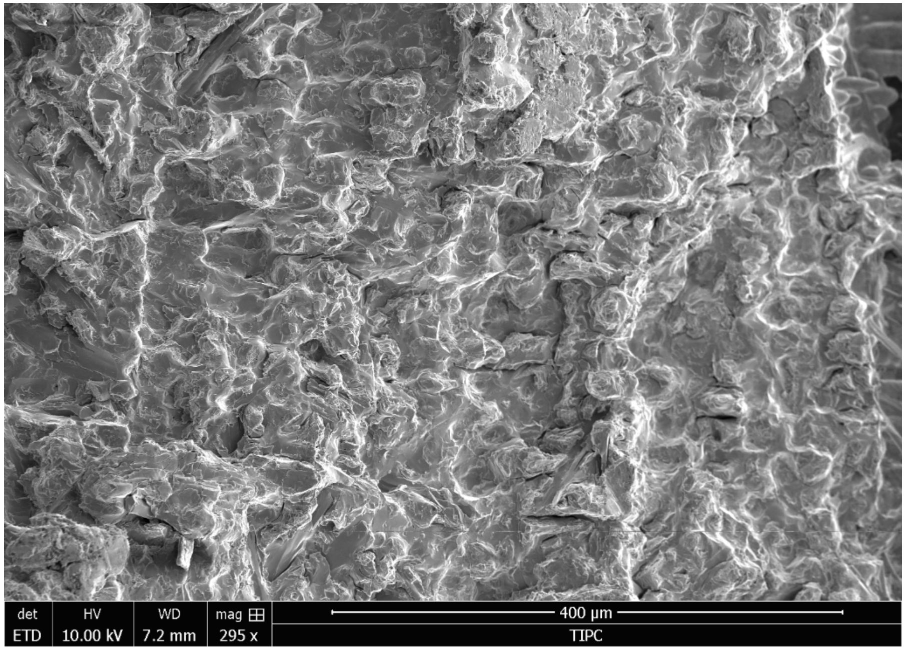
Morphology of fracture surface (fractured at 77K)



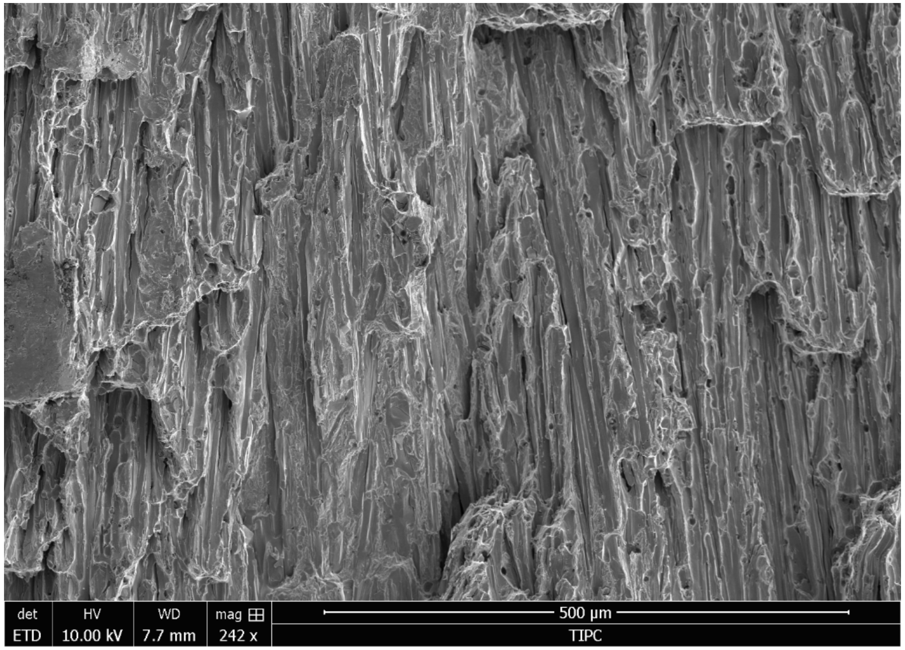




Comparison of morphology of fracture surface fractured at 293 K and 77 K



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.

thermoelectric materials

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Thermoelectric materials

Thermoelectric materials

Thermal energy ⇌ Electricity

↑

Transport of phonons and charge carriers

Advantages

1. Do not consume fossil fuel
2. Do not produce CO_2
3. No moving parts, no noise
4. Pollution-free

Applications

A car with themoelectric waste heat recovery system **BMW**

A portable refrigerator with a thermoelectric cooling system

Mars Exploration Rover “**Curiosity**”with thermoelectric generator powered by Isotope heat source

The Eco Thermal Drive watch **Citizen**

Preparation of thermoelectric materials

Thermoelectric (TE) materials $$ZT = \frac{\alpha^2 \sigma}{\kappa} T$$

α: Seebeck coefficient
σ: Electrical conductivity
κ: Thermal conductivity

Conventional methods for preparing bulk TE materials:

1.Growth from melt

2.Sintering from powder

Long-time heat treatment by furnace

➔ Much time and energy consumption

TE materials by combustion synthesis

Q: How to reduce the porosity?

A: Depress the formation and accelerate the removal of gas bubbles.

Two approaches of modified CS:

Clausius-Clapeyron Equation

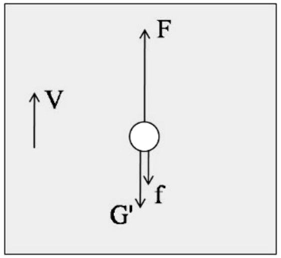
1.Gas-pressure combustion synthesis

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_V}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

2.High-gravity combustion synthesis

$$V = 2/9 \cdot \rho g r^2/\eta$$

Stokes' Equation



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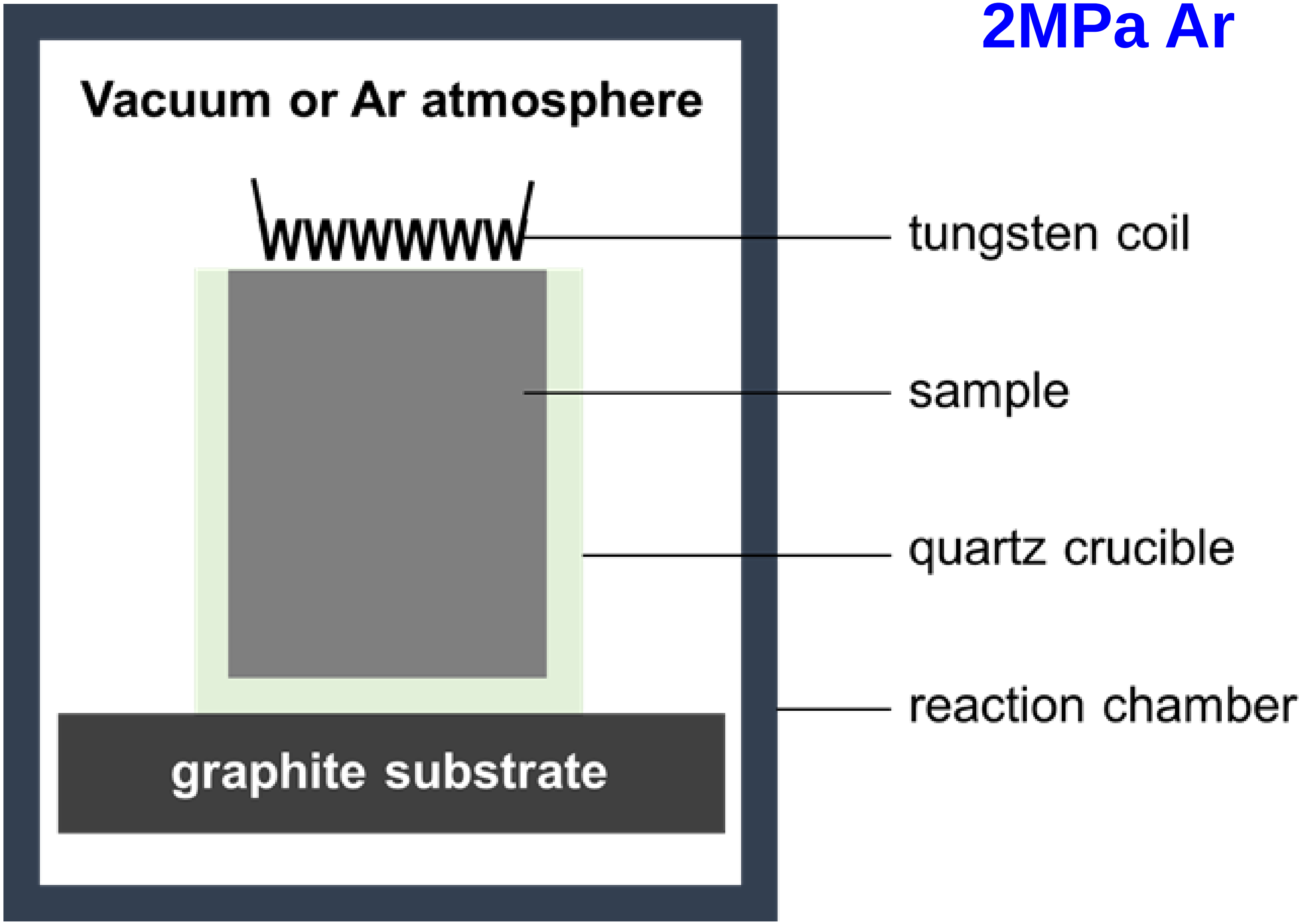
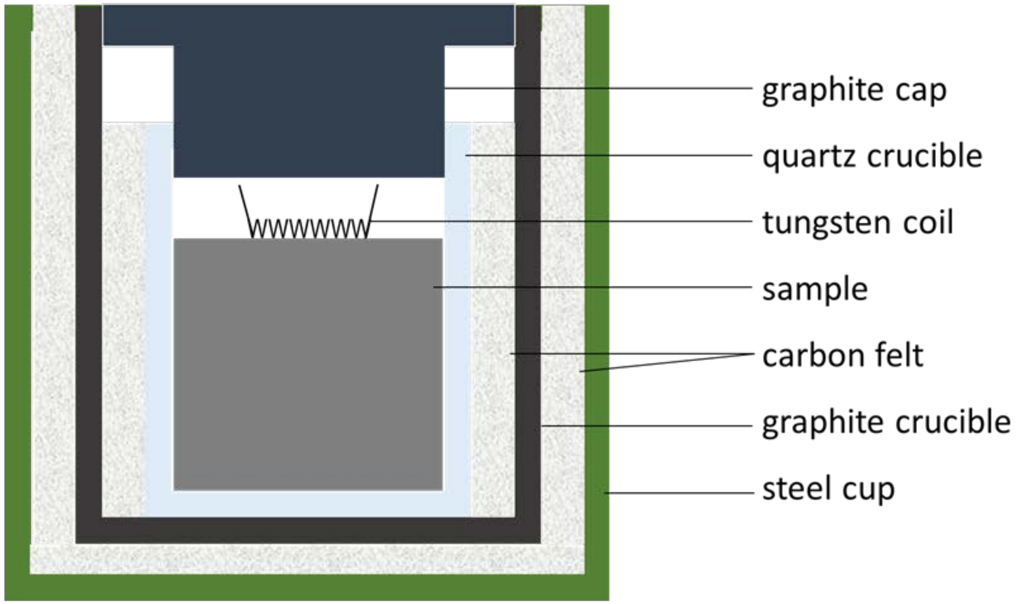
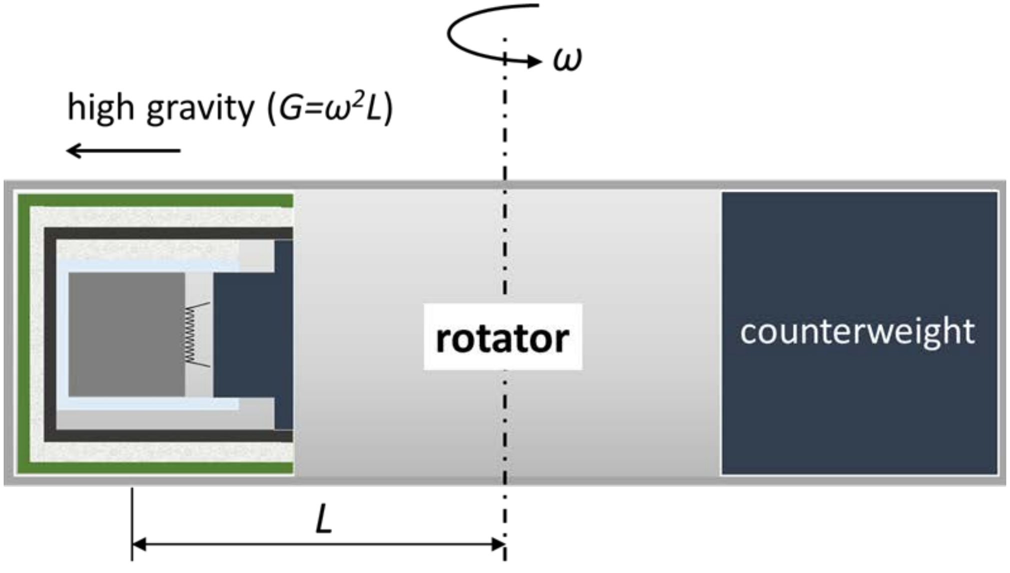
Gas-pressure combustion synthesis

2MPa Ar



High-gravity combustion synthesis





G=800 g

$g=9.8\ m/s^2$

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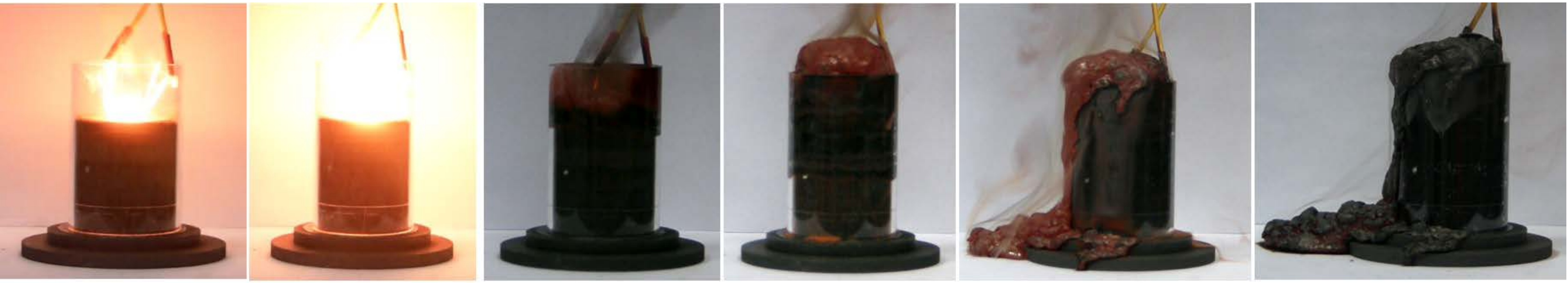
1. Cu_2SnSe_3

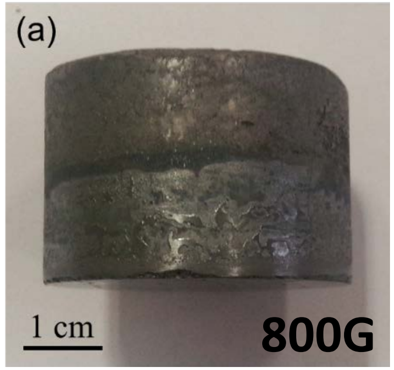
Reaction process in air

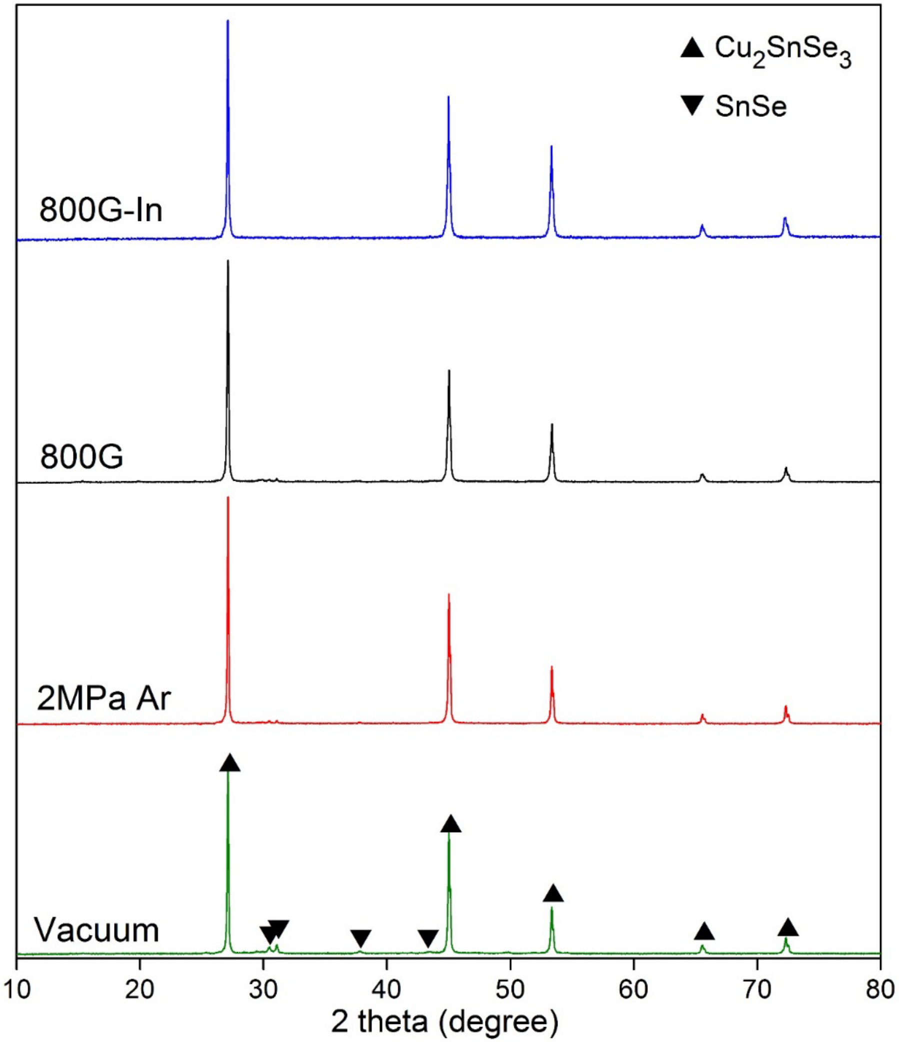
$$2Cu + Sn + 3Se = Cu_2SnSe_3$$

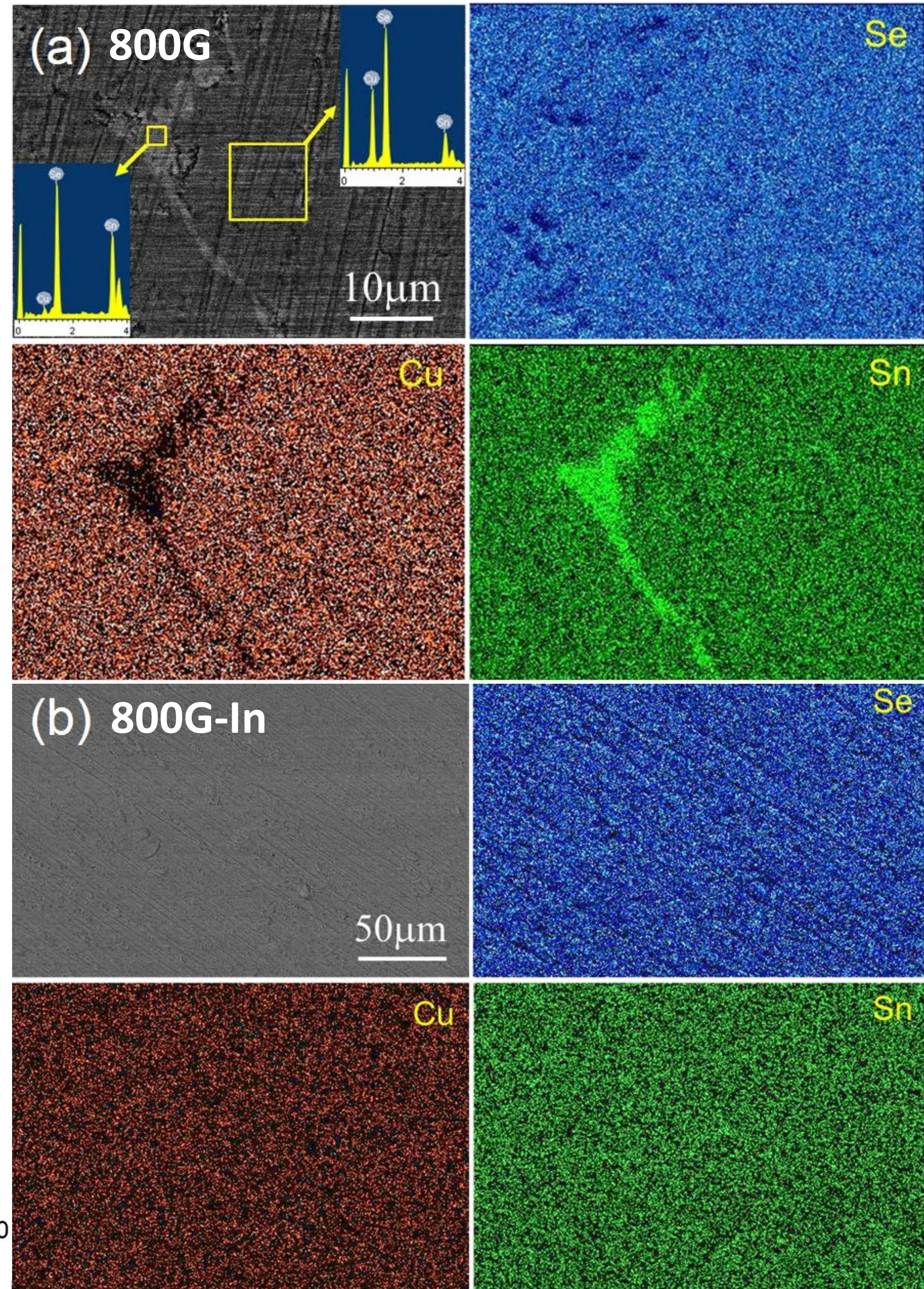


0 s   0 s   2 s   4 s   6 s   15 s

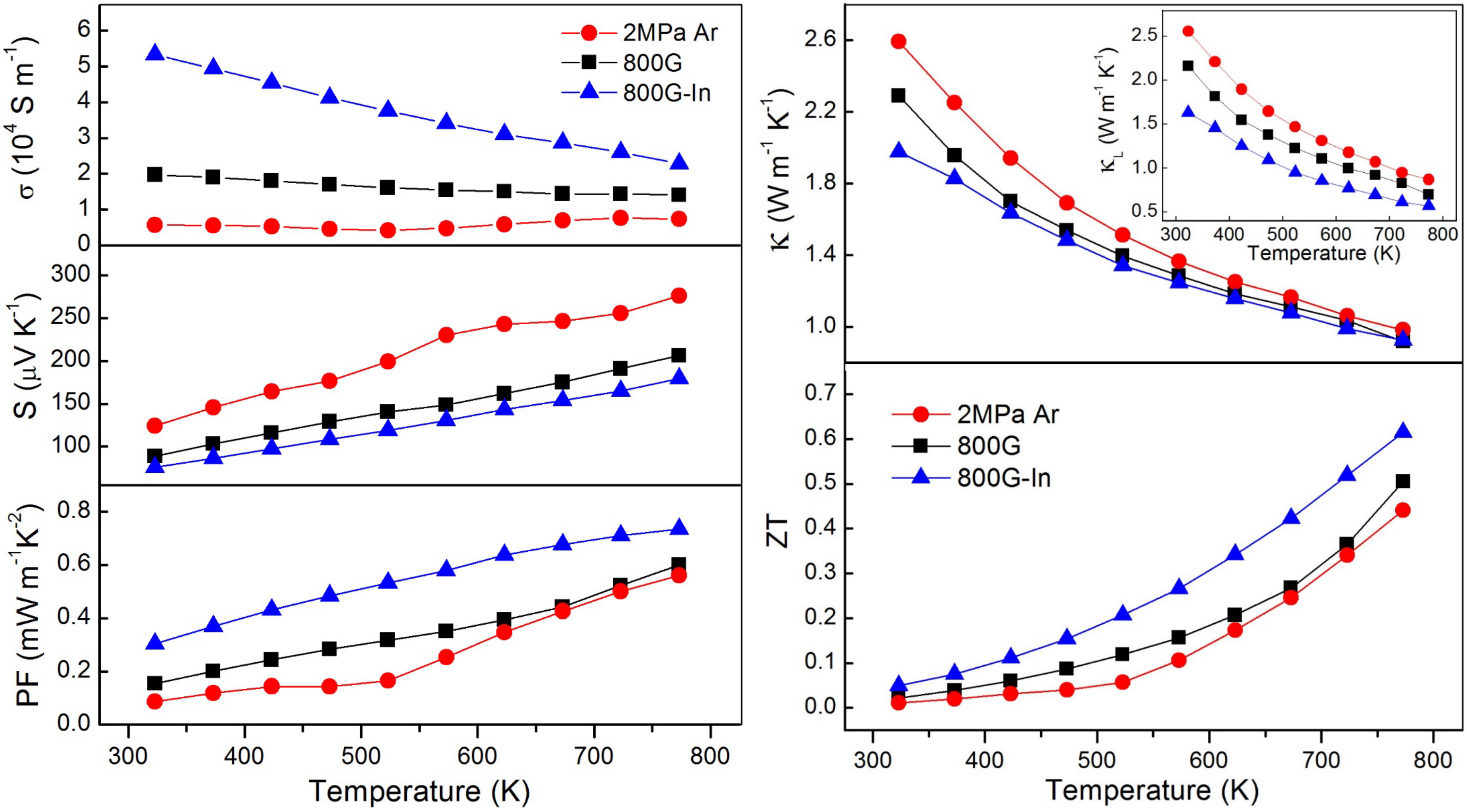
Bulk Cu_2SnSe_3 samples can be directly prepared by high-gravity or gas-pressure assisted combustion synthesis.







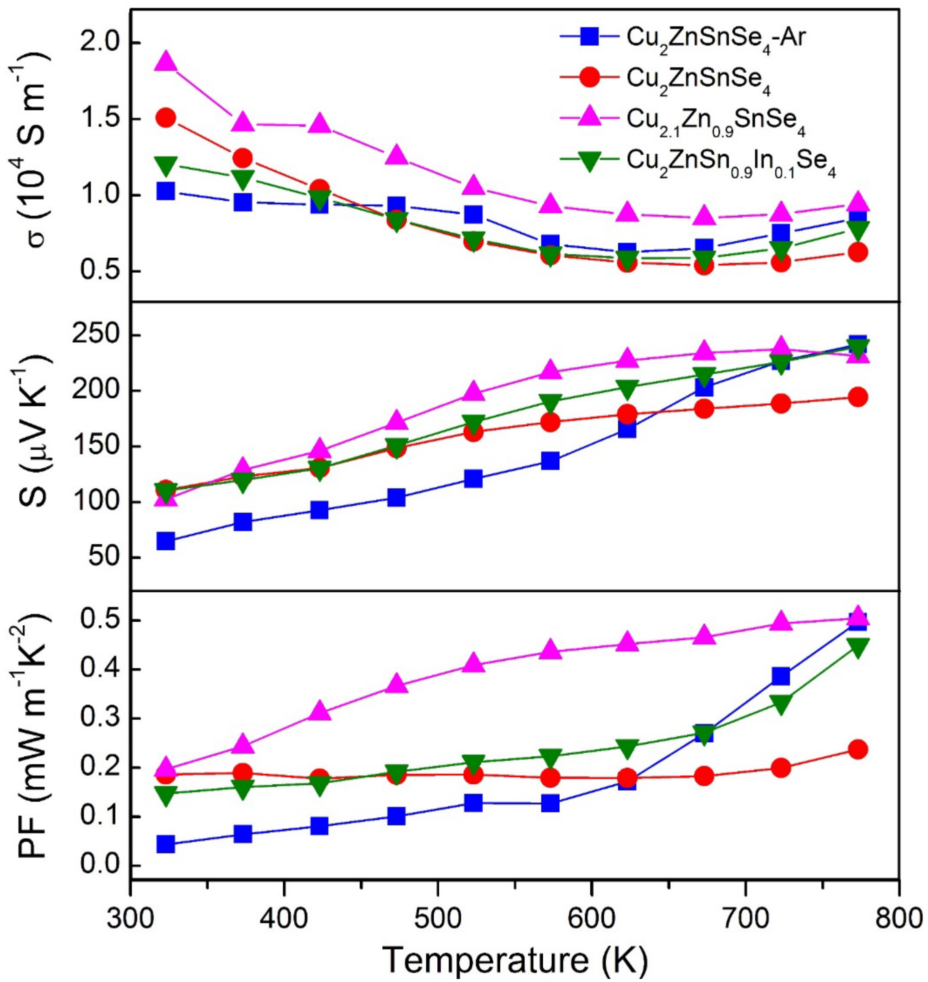
TE properties: comparable with sintered samples

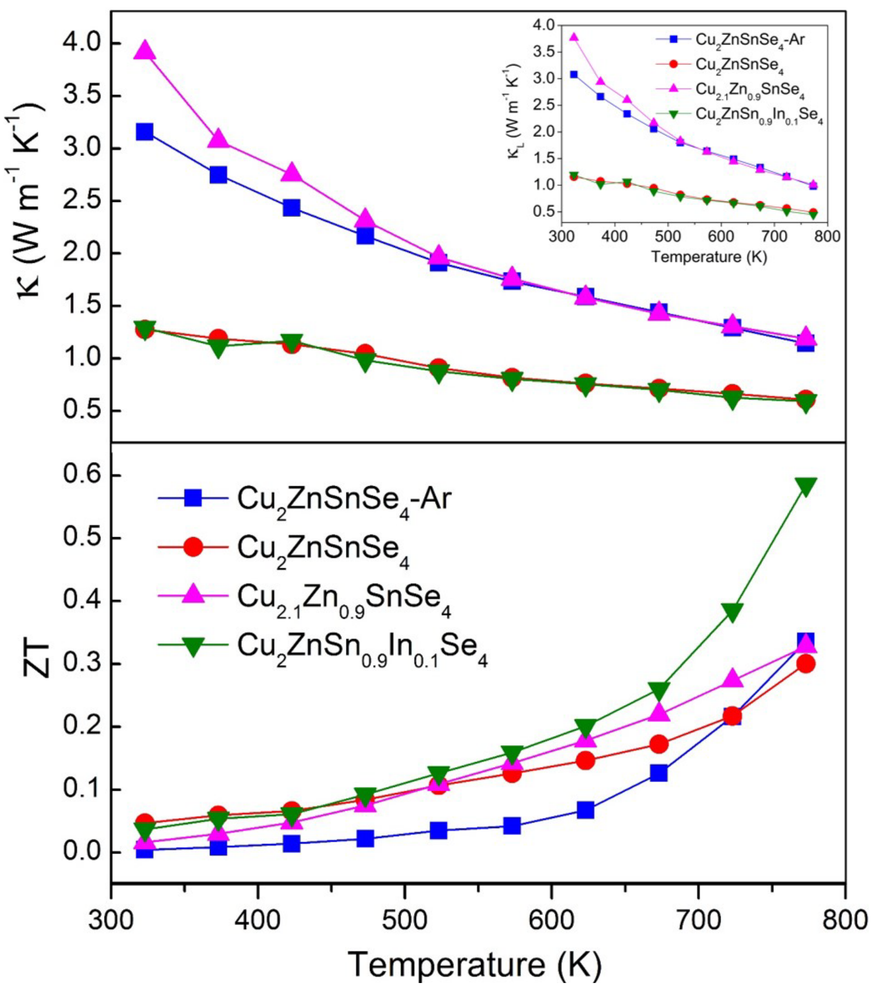


2. $Cu_2ZnSnSe_4$

$2Cu + Zn + Sn + 3Se = Cu_2ZnSnSe_4$

TE properties: comparable with sintered samples





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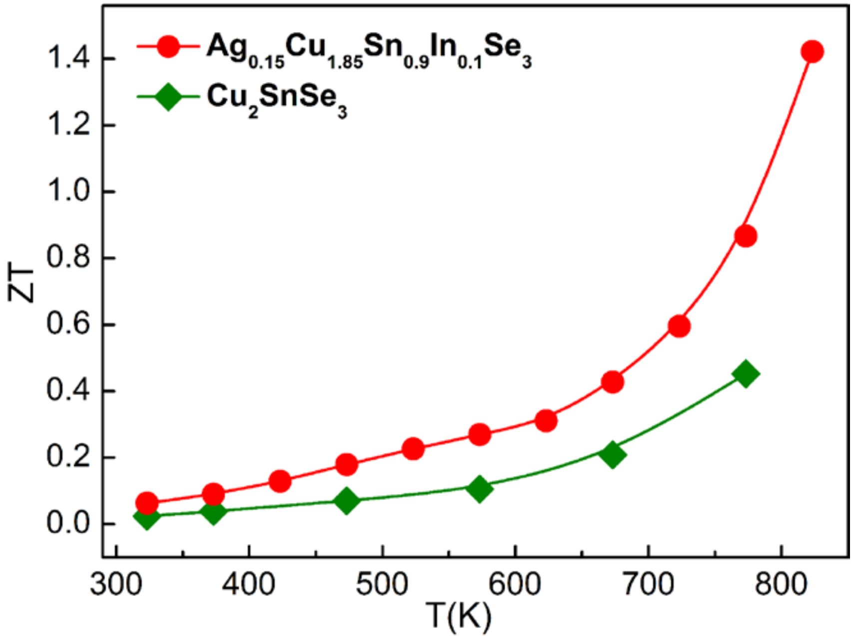
Combustion synthesis of thermoelectric materials

one-step, fast, furnace-free, scalable

- **Combustion synthesis offers an alternative approach to the fabrication of thermoelectric materials with much reduced processing time and energy consumption.**

- **The synthesized Cu_2SnSe_3 and $Cu_2ZnSnSe_4$ samples show thermoelectric properties similar to those prepared by the conventional methods.**

- **The thermoelectric properties can be optimized by doping.**



Thank you for your attention!