# Additive manufacturing of high-entropy alloys

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#### Introduction

(a) Conventional alloy Non-equiatomic HEA Equiatomic HEA Conventional alloy High entropy alloy B С (b) **Fig.** (a) The compositional range of conventional alloy 9% (blue region), non-equiatomic HEA (yellow region), 11% 45% and equiatomic HEA (red region) in a schematic ternary phase diagram of multicomponent alloy 34% systems, as well as an illustration of the atomic distribution of HEAs and common alloys (The boxed Based on Cantor Alloy (CA) Based on CA replacing one ellement with Al CA with one or more ellements replaced (different to Al) Refractory HEAs

black line displays ordered intermetallic/intermediate compounds, and each coloured dot represents a different type of element, and (b) Quantitative classification of AMed HEAs Source: <sup>(a)</sup> Source: Kim et al. 2020 [https://doi.org/10.1557/jmr.2020.140] <sup>(b)</sup>Torralba, and Campos 2020 [https://doi.org/10.3390/met10050639]

## **Cantor alloy**



**Fig.** (a) EBSD IPF map of a cross section of a single-layer LPBFed CA, (b) EBSD IPF map of a LPBFed CA cubic build, (c) and (d) SEM micrograph and its relevant EBSD IPF map of the build/substrate interface of LPBFed CA

Source: Piglione et al. 2018 [https://doi.org/10.1016/j.matlet.2018.04.052]

# **Cantor alloy**

**Fig.** (a) Cellular walls with nanoprecipitates in LPBFed CA, (b) Establishing that nanoprecipitates are  $Mn_2O_3$ , based on EDS line analysis (Blue, purple, red, light blue, yellow, and black circles and signs denote elements of Mn, Co, Cr, Fe, Ni, and O, respectively), (c) CA fatigue life curves after LPBF and after conventional processing, and (d) After failure, a dense cluster of deformation twins formed at the specimen surface



2 µm

#### Cantoralloy



**Fig.** Tensile engineering stress–strain curve of the LPBFed CA, tested at 293 K and 77 K

Source: Chen et al. 2018 [https://doi.org/10.3390/e20120937]

**Cantor alloy** 



**Fig.** An overview of CA processed using various manufacturing techniques, including casting, thermo-mechanical processing (TMP), spark plasma sintering (SPS), and AM

Source: Guan et al. 2021 [https://doi.org/10.1007/s11669-021-00913-w]

(a)

**Fig.** TEM micrographs of various AMed Al-modified Cas: (a)-(b) FCC precipitates in AlCoCrFeNi after ageing at 600°C for 168 h, (c)-(e) BCC (B2) precipitates (yellow circle) in the FCC matrix of AlCoCuFeNi after ageing at 1000°C for 10 h, and (f)-(g) L12 precipitates in  $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti_{0.3}$  after ageing at 750°C for 50 h



Source: <sup>(a),(b)</sup>Wang et al. 2017 [https://doi.org/10.1016/j.jallcom.2016.10.138] <sup>(c)-(e)</sup>Zhang et al. 2019 [https://doi.org/10.1016/j.msea.2018.11.118] <sup>(f)</sup>Lin et al. 2020 [https://doi.org/10.1016/j.addma.2020.101601]

**Fig.** Comparison of the microstructure of the cast and LPBFed AlCoCrFeNi HEA: (a) EBSD IPF map of the LPBFed as-built and (b) cast specimens (Cracks are marked with black arrows in the LPBFed asbuilt sample. The black boxes in (a) and (b) are the regions that are used to extract the samples for compositional analysis), (c) Atom probe tomography of the LPBFed as-built and (d) cast counterpart, showing the 3D distribution of the atoms Al, Co, Cr, Fe, and Ni, (e) 1D element concentration profile along the build direction of the LPBFed as-built, and (f) the cast counterpart.



Source: Han et al. 2020 [https://doi.org/10.1002/adma.201903855]

casting



Source: Yamanaka et al. 2020 [https://doi.org/10.1038/s41529-020-00127-4]

Fig. SEM micrographs of the LPBFed AlCrCuFeNix, showing crack mitigation by an increase in Ni content: (a) x =2.0, (b) x = 2.5, (c) x = 2.75, and (d) x = 3.0



Source: Luo et al. 2020 [https://doi.org/10.1016/j.addma.2019.100925]

**Fig.** (a) True tensile stress-strain curves of the as-cast and LMDed in various directions, as shown schematically (SD is the scan direction and DD is the deposition direction) of an AlCoCrFeNi<sub>2.1</sub> HEA, (b) and (c) SEM micrographs showing the fracture surface of the LMDed sample deformed in the scan direction





**Fig.** Engineering stress-strain curve of LPBFed FeCoCrNi HEA in the as-built state and annealed at various temperatures after printing

Source: Lin et al. 2020 [https://doi.org/10.1016/j.addma.2020.101058]



Fig. TEM micrographs of: (a) cellular structures, (b) magnified image of the red rectangle in (a) for C-HEA, (c) STEM micrographs indicating the presence of nanoprecipitates, (d) EDS mapping micrographs of both substitutional (Co, Cr, Fe, Mn, and Ni) and interstitial (O, C, and S) elements for the nanoprecipitates are shown in the TEM micrographs of the LPBFed C-HEA, and (e) Tensile properties of the C-HEAs and CA LPBFed with various processing parameters, as well as in the as-cast condition
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**Fig.** Engineering stress-strain curves of the LPBFed as-built and heat treated at 1393 K for 3 hours followed by air cooling (ST A.C.) or water quenching (ST W.Q.), as well as EBMed and heat treated (similar heat treatment scheme with LPBFed samples) samples of CoCrFeNiTi<sub>7</sub>Mo<sub>3</sub> HEA



Source: Fujieda et al. 2019 [https://doi.org/10.1016/j.addma.2018.10.023]



ണംഭ

Deformed

Substructured

200 mm

Recrystallized

**Fig.** (a) Stress-strain curves of LPBFed FeCoCrNi HEA deformed at various temperatures with a strain rate of 5×10<sup>-3</sup> min<sup>-1</sup>. Serrations during deformation at 400 and 500°C are indicated with arrows and shown in the magnified inset, Recrystallization maps indicating recrystallized (blue), substructured (partially recrystallized, yellow), and deformed (red) grains in the deformed samples at (b) 400°C, (c) 600°C, and (d) 800°C (GND density (pGND) is also shown in the insets)

Source: Lin et al. 2022 [https://doi.org/10.1016/j.msea.2021.142354]

800 °C

**Refractory high-entropy alloys** 



Fig. (a) Solidification path calculated by Thermo-Calc and (b) crack susceptibility index of NbMoTaX alloys

Zhang et al. 2021 [https://doi.org/10.1016/j.matdes.2021.109462]

# **Refractory high-entropy alloys**

**Fig.** (a) TEM micrograph of the interstitial phase in NbMoTaTi alloy, (b) the fracture of GB phase in NbMoTaTi alloy under stress F, and (c) stacking faults in GB phase of NbMoTaTi0.5Ni0.5



Zhang et al. 2021 [https://doi.org/10.1016/j.matdes.2021.109462]

### **Refractory high-entropy alloys**



**Fig.** Compressive stress-strain curves of LPBFed NbMoTaTi<sub>0.5</sub>Ni<sub>0.5</sub> HEA at room and elevated temperatures

Zhang et al. 2021 [https://doi.org/10.1016/j.matdes.2021.109462]

## **Refractory high-entropy alloys**



**Fig.** Summary of microhardness of the commonly reported RHEAs produced by LMD, LPBF, and casting

#### Summary

**Fig.** Yield strength elongation of various HEAs and Al alloys produced via various AM techniques and casting

