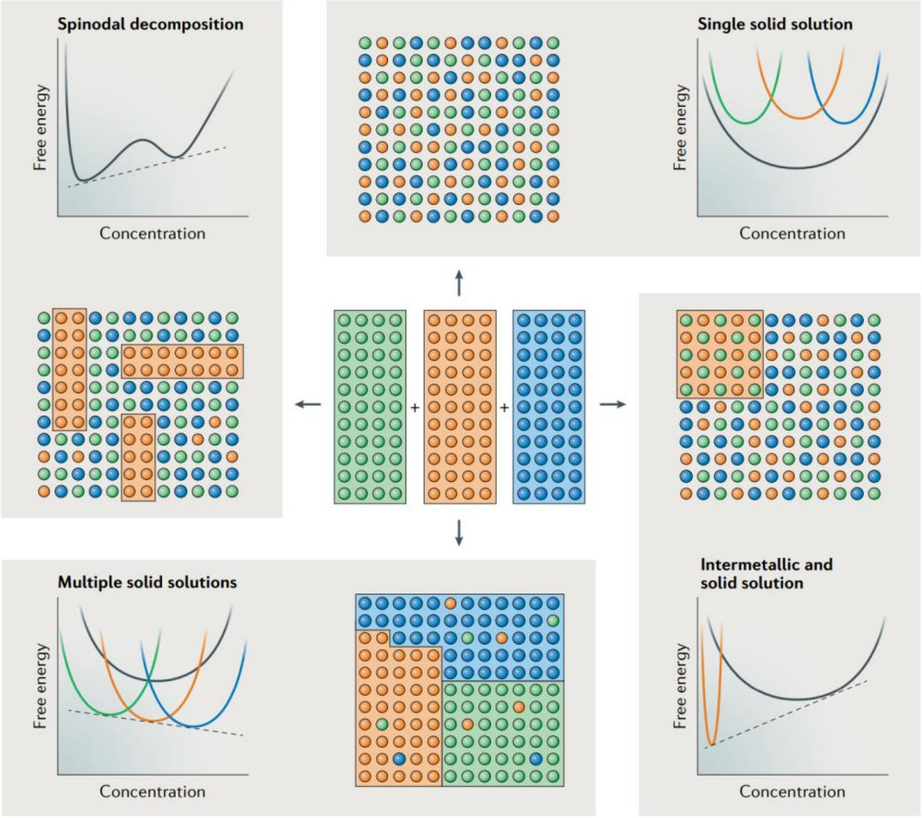
High entropy alloys for nuclear applications

- Outline
  - What are high entropy alloys?
  - What are expected properties?
  - Where we are at time in the development?
    - State of the Art, HEAFNA
  - What are the required next steps?
    - open issues, gaps, international cooperations

HEA, CCA, Multiphase alloys, …..

Three alloying elements – possible mixing reactions



Easo P. George, Dierk Raabe and Robert O. Ritchie
Nature reviews | Materials volume 4 | AUGUST 2019

$$A + B = AB \text{ (solution)}: \Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$A + B = AB \text{ (intermetallic)}: \Delta G_f = \Delta H_f - T\Delta S_f$$

$$\Delta S_{mix} = -R\Sigma x_i \ln x_i$$

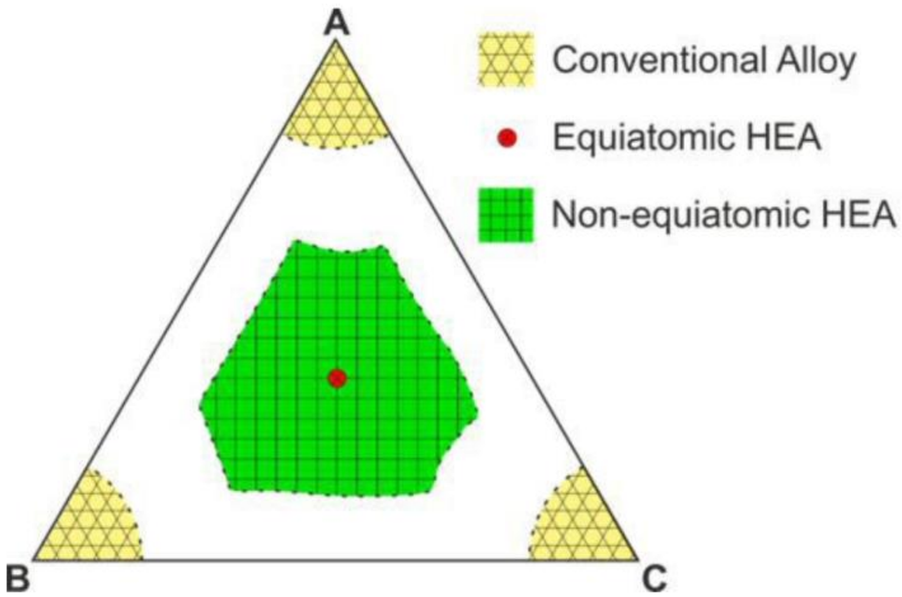
$$\Delta S_{mix} = R\ln n$$

HEA=five or more elements in equiatomic concentrations

Yeh, J. W. et al. Adv. Eng. Mater. 6, 299–303 (2004).

High mixing entropy combined with low mixing enthalpy to avoid intermetallics
➔ Stable Solid Solutions

HEA, CCA, Multiphase alloys, …..



The strict rule of equiatomic was eased

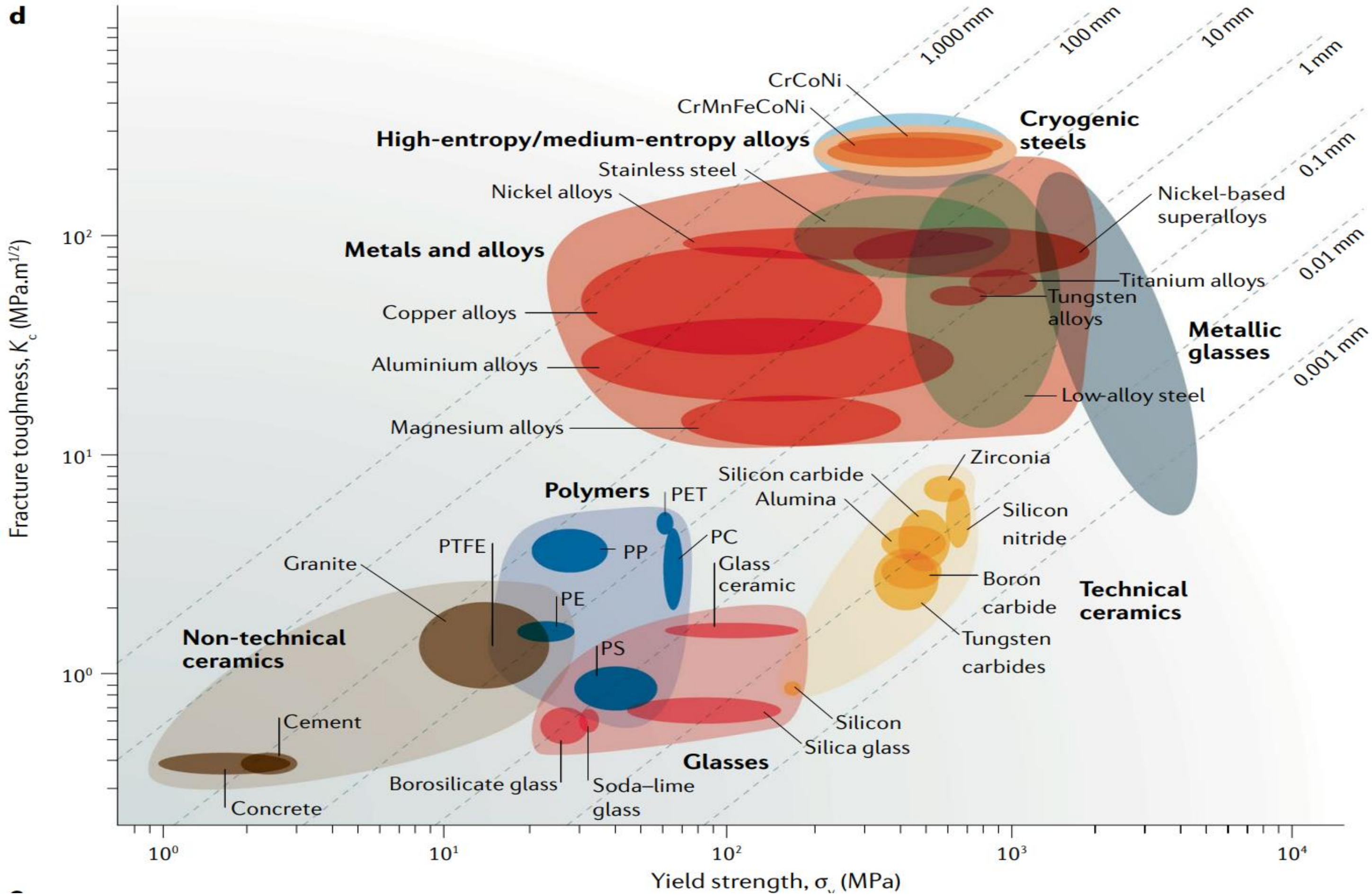
for 5at%<x<35at% for each constituent

This opens a wide field of potential alloys

High distortion of the lattice due to the different atoms sizes
Sluggish (slow) diffusion
High entropy effect to stabilise the solid solution
Properties arise from a "cocktail"effect, reaching unusual levels

What properties are expected?

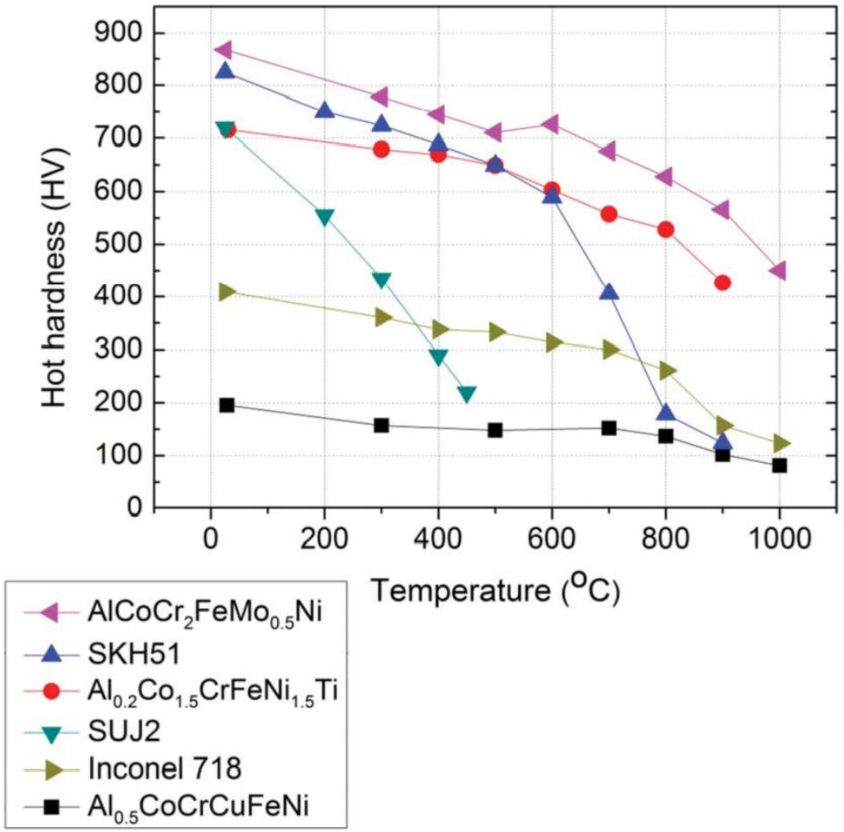
Exceptional mechanical properties of a few specific alloys, most notably the FCC CrCoNi-based alloys

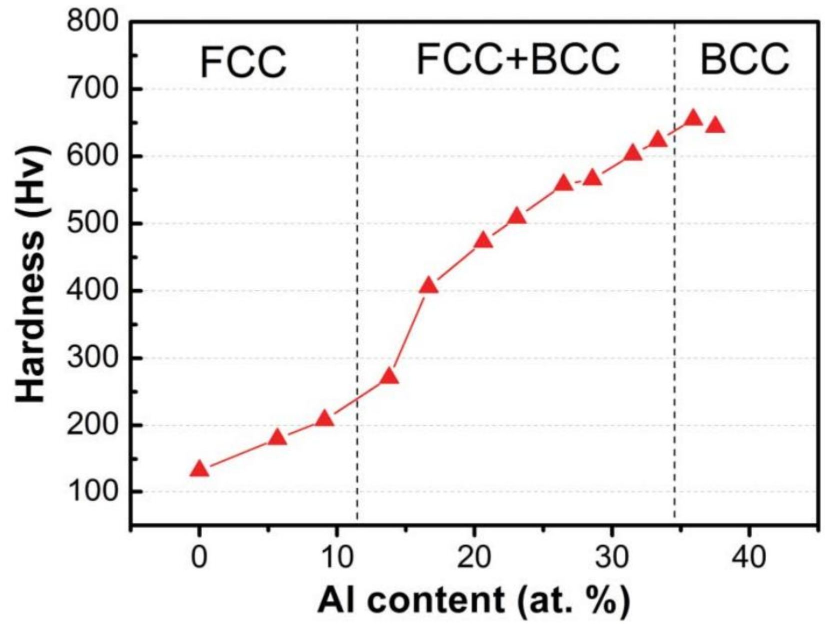


What properties are expected?

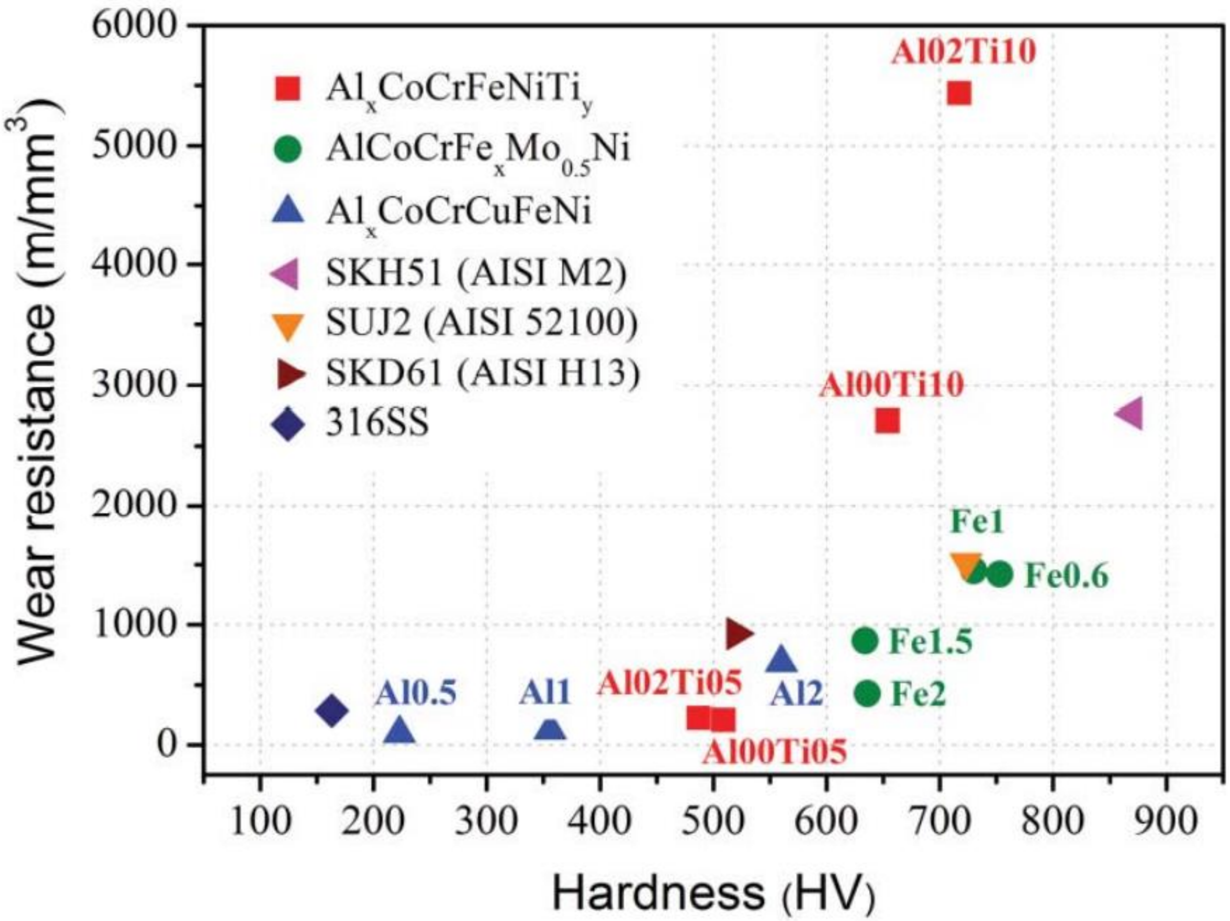
High Hardness even at high temperatures

Mater. Res. Lett., 2014





What properties are expected?



Ming-Hung Tsaia and Jien-Wei Yeh - Mater. Res. Lett., 2014 Vol. 2, No. 3, 107–123, http://dx.doi.org/10.1080/21663831.2014.912690

Properties expected for nuclear application

- Survive extreme conditions
  - Temperature, Corrosion, Stress, Heat flux, ….
  - + Irradiation

  - Reduced or low activation → no Co - Fusion community
  - Reduced or low neutron cross section

- Potential Use:
  - ATF – GENII – III –
  - Cladding - Structural materials GenIV, …..
    - Wear resistance, …

Some irradiation related HEA research from literature

- Reported improved irradiation resistance
  - (i) higher resistance to irradiation defect formation [47–50],
  - (ii) lower void swelling in comparison to conventional alloys [51–53],
  - (iii) higher microstructural stability (usually phase stability) than conventional alloys under irradiation [49,51,52,54,55]
- Potential explanations
  - (i) the effect of reduced thermal conductivity on cascade dynamics
  - (ii) the effect of sluggish diffusion on damage accumulation
  - (iii) the effect of defect formation energies on damage accumulation mited irradiation hardening [51].
- BUT
  - No consistency in observed effects – requires systematic irradiation studies
  - And dedicated design of HEA materials

Pickering, E.; Carruther, A.; Barron, P.; Middleburgh, S.; Armstrong, D.; Gandy, A. High-Entropy Alloys for Advanced Nuclear Applications. Entropy 2021, 23, 98. https://doi.org/10.3390/ e23010098

State of the Art – HEAFNA, and more?

Officially started Febr. 2019

WP1 Modelling, design, production and basic characterization (microstructure & mechanic properties)

CENIM

WP2 HEA Compatibility with coolants

KIT

WP3 High temperature mechanical tests & post-experiment characterization + modelling

CIEMAT

WP4 Irradiation tolerance of HEA

HZDR

WP5 Fundamental understanding of irradiation in HEAs

SCK-CEN

Coordinated by KIT
24 Partners from 13 Countries

837 PM 8 Mill. € in total – all- inkind

(2018-2022) HEAFNA: High entropy alloys

Work plan - as written in the proposal

WP1: Modelling, design, production and basic characterization (microstructure & mechanic properties) – CENIM, KIT, CENIM, IMP, IC, NSC-KIPT, NIMP, AALTO, CEA-DEN, AALTO, CEIT (?)

Modelling, Design and Production:

Casting (arc or induction melting), **PM** (SPS), L**aser-melting**, **Additive manufacturing**

Basic characterization: Microstructure and thermophysical properties(XRD, SEM, TEM, APT, ..);

Basic mechanical tests: Nanoindentation for screening

WP2: HEA compatibility with coolants – KIT, CV-REZ, CIEMAT, CNRS-UMET, CEA-DEN, USTUTT, Polito

Compatibility tests:

Coolants: molten metals; molten salts; steam-accidental conditions (Gen II, III), SCW; He, air; Supercritical CO_2

Post corrosion examination of compatibility

Corrosion mechanism and modelling

(2018-2022) HEAFNA: High entropy alloys

Work plan - as written in the proposal

WP3: High temperature mechanical tests & post-experiment characterization + modelling – CIEMAT, HZDR, VTT, CNSR/UMET, RATEN ICN, MPA, CVR, NIMP, KIT

Mechanical tests: small punch; ring and pin-load; creep-fatigue; bending

If sufficient material is available: creep, low cycle fatigue, fracture toughness, ……

Thermal ageing – microstructural and phase stability + mechanical behaviour after ageing

XTD; TEM; SEM-EBDS; SANS; APT; XRF+XANES; XRF+SIMS; …..

In-situ deformation and annealing (SEM, TEM)

SMALL PUNCH CREEP; NANOINDENTATION; HARDNESS

WP4: Irradiation tolerance of HEA - HZDR, AALTO, CIEMAT, CNRS/GPM, PSI, STUBA, IC, NCSKIPT

Ion irradiation - heavy and light ions

Post irradiation examination – TEM; SEM; APT; PAS; X-Ray; Nanoindentation; Tensile; ..

Modelling

WP5: Fundamental understanding of irradiation in HEAs – SCK-CEN, EDF, KTH, UHELSINKI

Interatomic potentials, cascades simulations, thermodynamics (DFT, VASP, ….)

HEAFNA

- Very large project

  ➔ WP‘s are managed individually by the WP leader

- Project coordination mainly links the WP‘s

- WP1 and WP2 started in 2019
  - WP1 meeting and first exchange on pre-selection
  - WP2 some corrosion work by KIT
  - WP4 some work by NCSKIPT

Status of work

WP1: Modelling, design, production and basic characterization (microstructure & mechanic properties) – CENIM, KIT, CENIM, IMP, IC, NSC-KIPT, NIMP, AALTO, CEA-DEN, AALTO, CEIT

Different families of HEA that are considered in the PP are discussed

Family 1: FeNiCrMn family with additions of Cu, Mo and others

Family 2: FeCrNi family with additions of Al and Pd

Family 3: TiZrHfCoNiCu - only for comparison (WP4 irradiation and modelling)

Family 4: A refractory family (not defined), in the range (or around) the well known MoNbTaVW

Methodology to down select compositions discussed and agreed

Family 1 and Family 2 are explored

Thermocalc simulations on family 2 started – to be continue with Family 1, 3 and 4

First HEAs from "family 2+Al" produced and their thermo-physical properties characterized

Modelling, Design, Criteria for HEA model alloy selection

$$\Omega = \frac{\sum c_i T_{m,i} \cdot \Delta S_{mix}}{|\Delta H_{mix}|} \quad \Omega > 1.1 \quad \Delta H_{mix} = \sum_{j>i}^{n} 4 H_{ij} c_i c_j$$ -15 kJ/mol < ΔH_{mix} < 5 kJ/mol

$$\delta_r = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}$$ 1% < δr < 6.6% $$VEC = \sum c_i \cdot VEC_i$$ VEC > 7.5 for FCC

Microstructure	ΔH_{mix} (KJ/mol)	δr (%)	Ω	VEC
FCC solid solution	$-15<\Delta H_{mix}<5$	$1< \delta r <6.6$	>1.1	>7.8
FCC+IM	$-15<\Delta H_{mix}<5$	$1< \delta r <6.6$	>1.1	7.5 < VEC < 7.8
FCC+BCC+IM	$-15<\Delta H_{mix}<5$	$1< \delta r <6.6$	>1.1	6 < VEC < 7.5

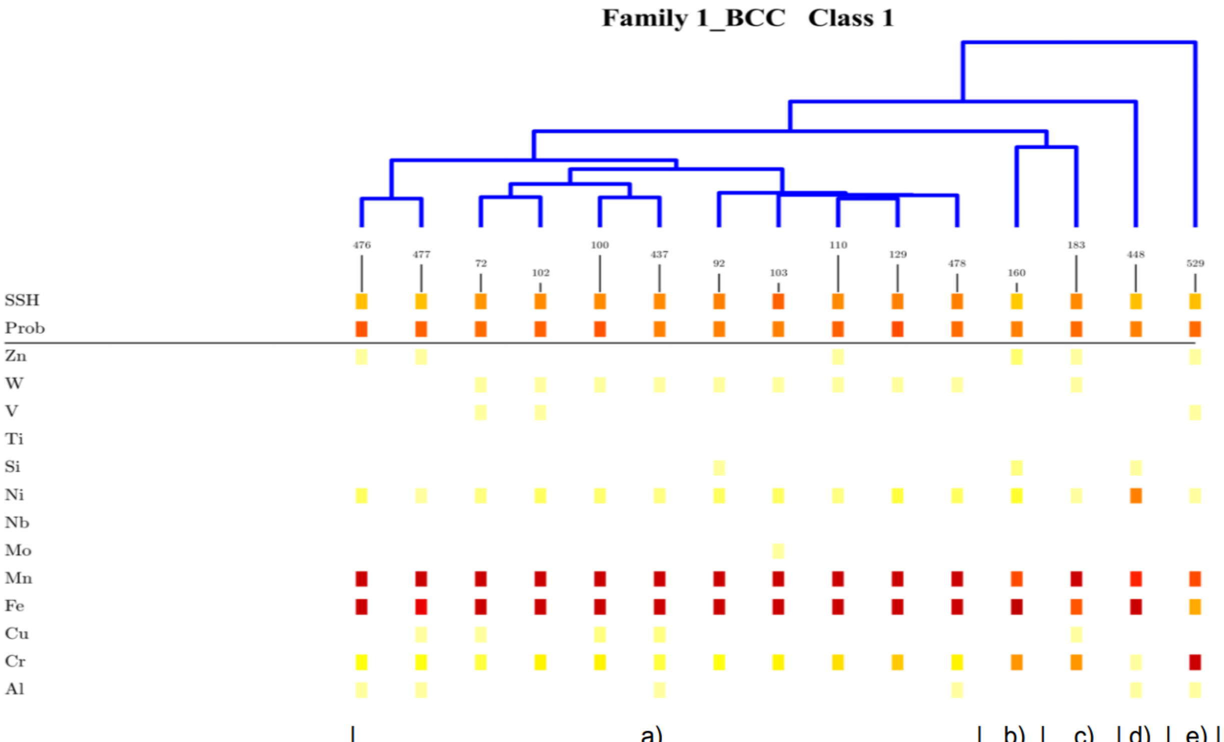
Yang et al. Mater. Chem. Phys. 132 (2012) 233-238. Guo et al. J APPL PHYS.109 (2011) 103505.
Zhang et al. Adv. 10 (2008) 534-538.

Screening of potential HEA's

Family 1 – BCC – Class 1

(High Probability of Solid solution, low yield strength)

Isaac Toda-Caraballo,
David San Martin
CENIM-CSIC

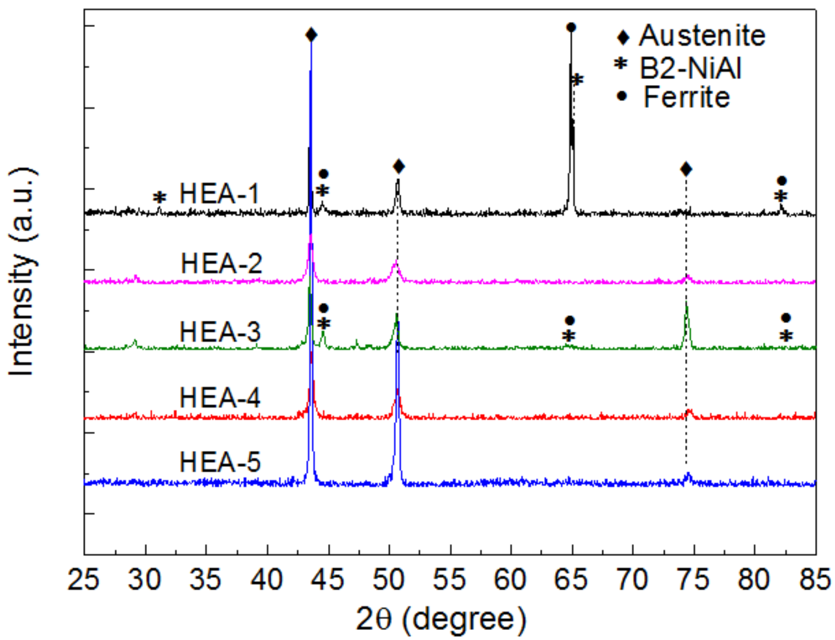


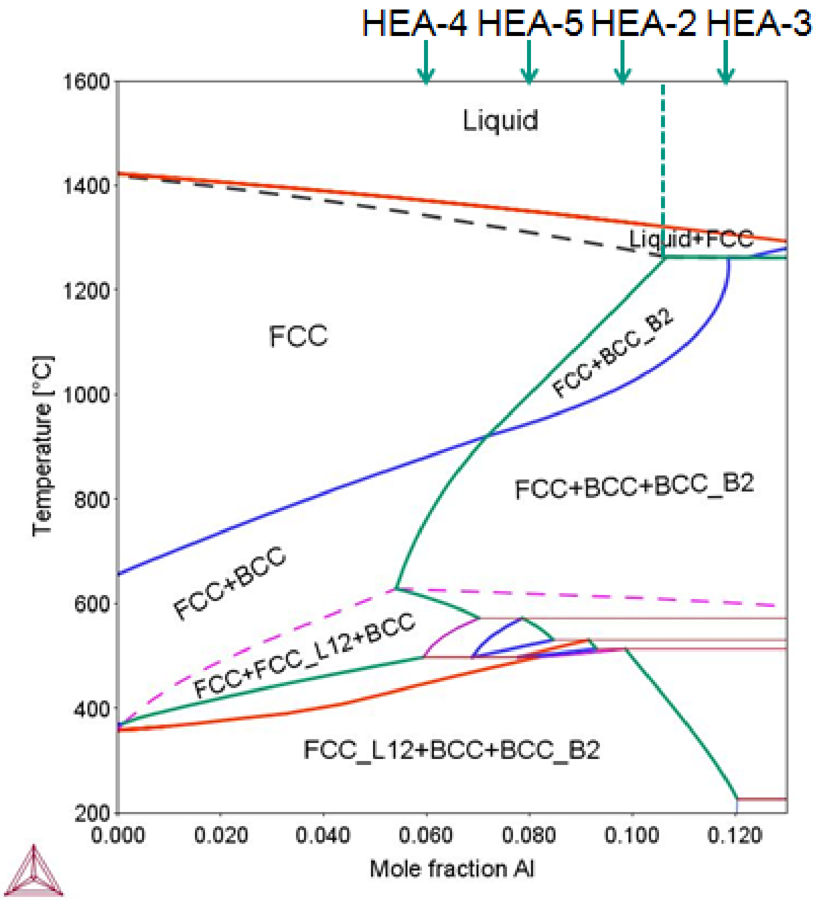
Family 1 – BCC – Class 1 Alloy 1:	Fe7 Mn7 Cr3 Ni2	Al, Cu, Mo, Si, V, W, Zn
Family 1 – BCC – Class 1 Alloy 2	Fe7 Mn5 Cr4 Ni2 Si5 Zn	
Family 1 – BCC – Class 1 Alloy 3	Mn7 Fe5 Cr4 Cu5 Ni5 W5 Zn5	
Family 1 – BCC – Class 1 Alloy 4	Fe7 Mn6 Ni4 Al1 Cr1 Si1	
Family 1 – BCC – Class 1 Alloy 5	Cr7 Mn5 Fe4 Al1 Ni1 V1 Zn1	

Alumina forming HEA Alloys - Pb alloys

Nominal composition of HEA alloys, and values of parameters used for HEA design.

Code	Nominal Composition (at.%)	ΔH_{mix}	*VEC*	*δr*	*Ω*	Predicted Phase
HEA-1	$Al_{9.76}Cr_{30.28}Fe_{32.95}Ni_{26.91}$	-8.62	7.56	4.44	2.28	FCC+IM
HEA-2	$Al_{9.85}Cr_{22.50}Fe_{34.50}Ni_{33.15}$	-8.29	7.75	4.41	2.31	FCC+IM
HEA-3	$Al_{11.69}Cr_{22.40}Fe_{32.62}Ni_{33.29}$	-8.87	7.62	4.74	2.18	FCC+IM
HEA-4	$Al_{6.02}Cr_{25.01}Fe_{33.99}Ni_{34.98}$	-6.84	7.89	3.54	2.76	FCC
HEA-5	$Al_{7.96}Cr_{23.23}Fe_{34.06}Ni_{34.75}$	-7.55	7.85	4.02	2.52	FCC





Calculated phase compositions of as cast $Al_xCr_{0.68}FeNi$ (x: 0-0.4) as a function of Al content, calculated by Thermo-calc, TCHEA4 database

Status of work

WP2: HEA compatibility with coolants – KIT, CV-REZ, CIEMAT, CNRS-UMET, CEA-DEN, USTUTT, Polito

Compatibility tests:

Coolants: molten metals; molten salts; **steam-accidental conditions** (Gen II, III), SCW; He, air; Supercritical CO_2

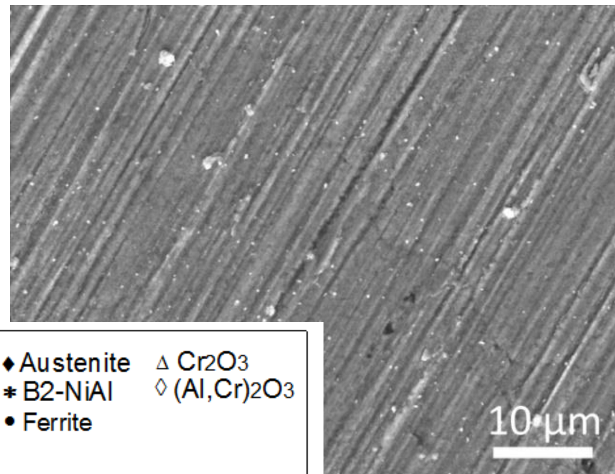
Post corrosion examination of compatibility

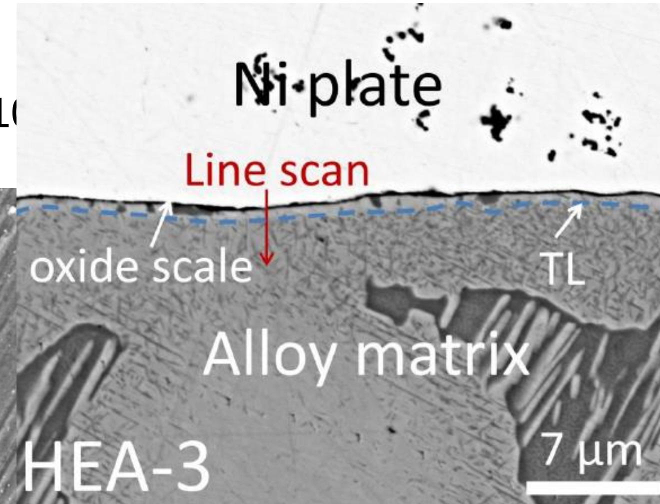
Corrosion mechanism and modelling

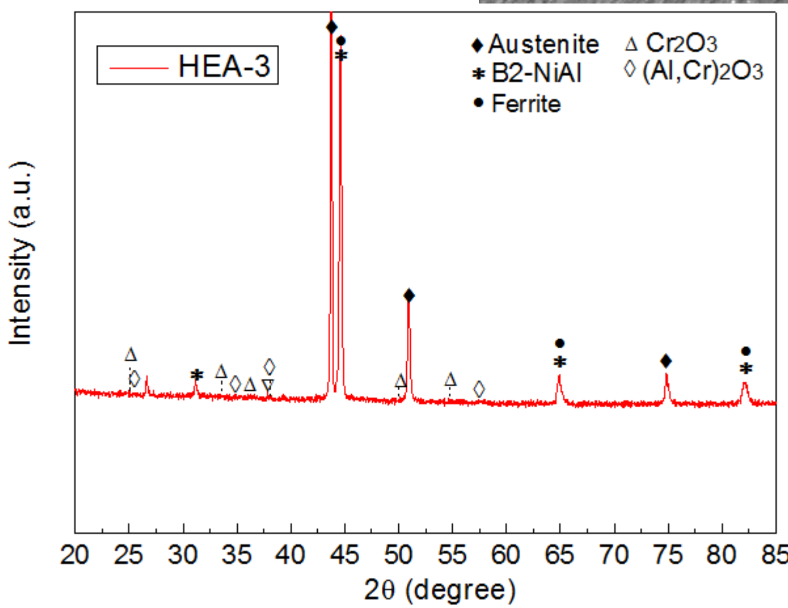
Corrosion of HEA alloys in molten Pb (600 °C)

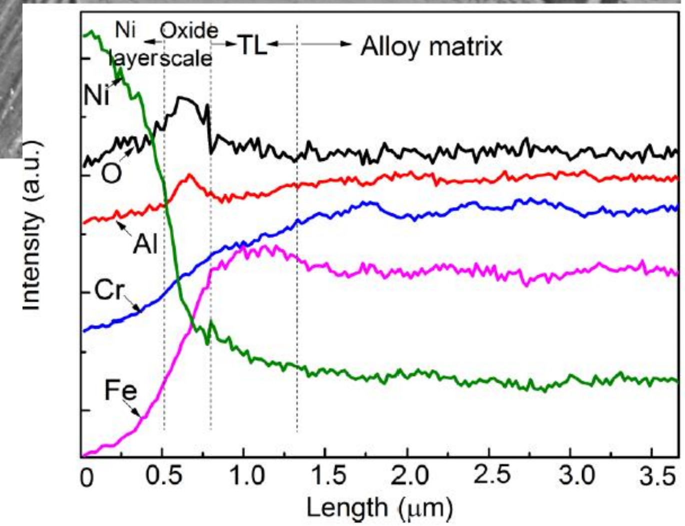
Experimental condition:

10^{-6} wt.% oxygen containing molten Pb at 600 °C for 1(and **2000 h**.





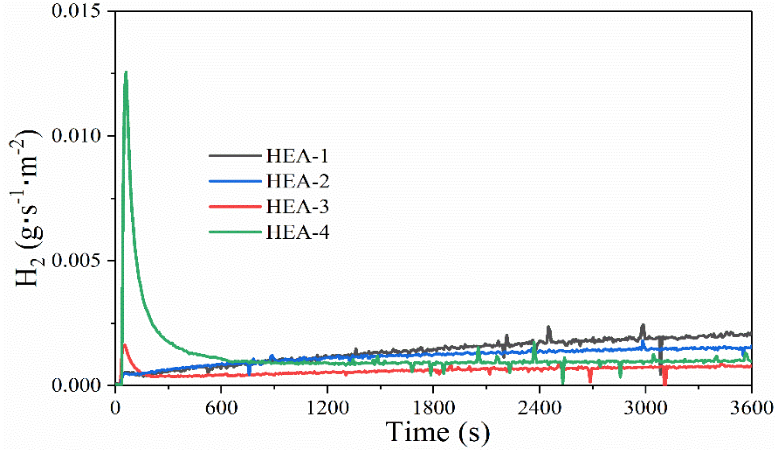


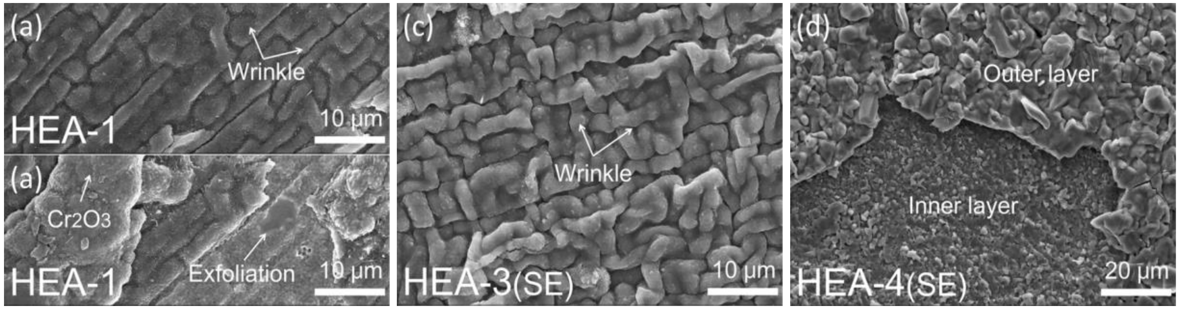


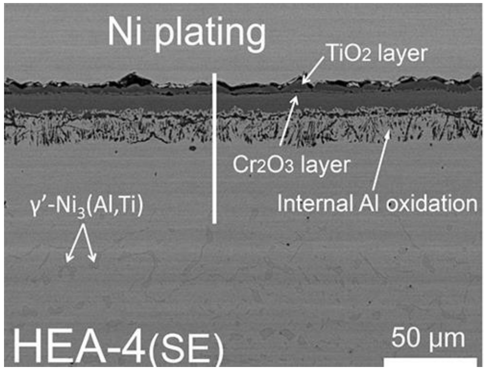
TL: transitional layer

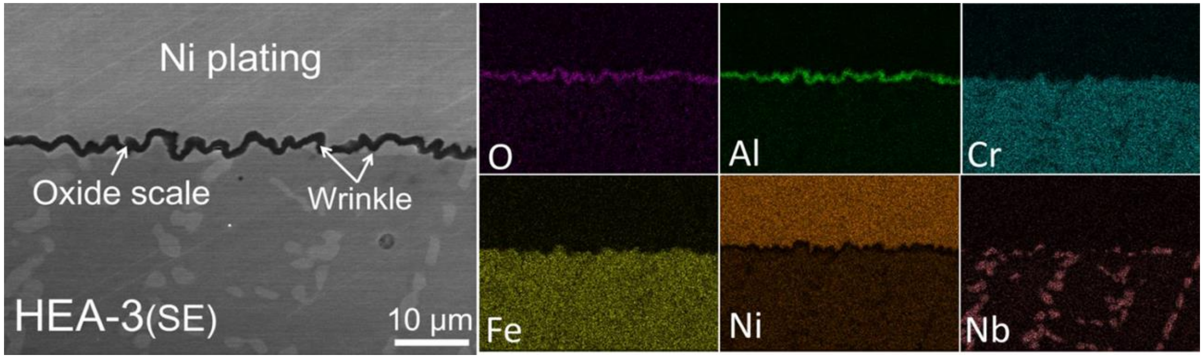
Isothermal steam test at 1200°C 1h HEA

Code	Nominal composition (wt.%)	Mass gain (g/m^2)
HEA-1	$Al_{7.9}Cr_{23.2}Fe_{34.1}Ni_{34.8}$	3.89
HEA-2	$Al_{8.9}Cr_{23.1}Fe_{33.7}Ni_{34.3}$	2.37
HEA-3	$Al_{8.2}Cr_{21.4}Fe_{30.3}Ni_{35}Nb_{5.1}$	7.2
HEA-4	$Al_{7.9}Cr_{22}Fe_{31.9}Ni_{33.2}Ti_5$	26.56









All form alumina scales
Nb improves scale adhesion
Ti ➔ internal oxidation

H. Shi, Ch. Tang, A. Jianu, R. Fetzer, A. Weisenburger, M. Steinbrueck, M. Grosse, R. Stieglitz, G. Müller, Corrosion (2020) 170, 108654

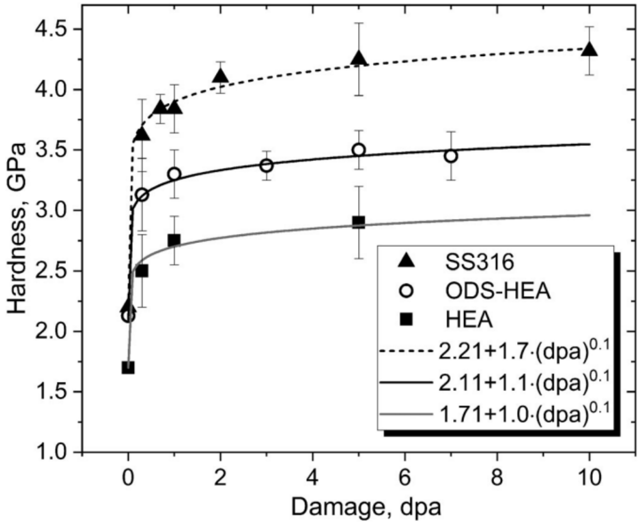
Ion irradiation - heavy and light ions

Post irradiation examination – TEM; SEM; APT; PAS; X-Ray; Nanoindentation; Tensile; ..

Modelling

20Cr–40Fe–20Mn–20Ni, ODS–20Cr–40Fe–20Mn– 20Ni

1.4 MeV argon ions at room temperature (RT) in a dose range of 0.1–10 dpa.



Reduced irradiation hardening

V.N. Voyevodina,b, S.A. Karpova , G.D. Tolstolutskayaa , M.A. Tikhonovskya , A.N. Velikodnyia , I.E. Kopanetsa , G.N. Tolmachovaa , A.S. Kalchenkoa , R.L. Vasilenkoa and I.V. Kolodiy, Effect of irradiation on microstructure and hardening of Cr–Fe–Ni–Mn high-entropy alloy and its strengthened version, PHILOSOPHICAL MAGAZINE https://doi.org/10.1080/14786435.2019.1704091

What are next steps?

- Open issues, gaps?
  - Understanding of HEA irradiation response
  - Improved modelling – for pre-selection
  - Mechanical testing – long term phase stability -
- Looking for a funded project
  - NUGENIA together with EERA-JPNM
  - Discussions started end of last year
  - Waiting for the final EURATOM call text
- HEA workshop organized by EGISM
  - Expert Group on Innovative Structural Materials
  - Collection of ideas and potential topics and speackers