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REFRACTORY AND LIGHT WEIGHT HIGH ENTROPY ALLOYS FOR INDUSTRIAL APPLICATIONS

Félix Royer^{1,2}, Marie Erbeia^{1,2}, Jaâfar Ghanbaja¹, Abdelkrim Redjaimia^{1,2}

¹Institut Jean Lamour UMR CNRS 7198, Université de Lorraine, F-54011 Nancy, France

²Ecole Européenne d'Ingénieurs en Génie des Matériaux, F-54010 Nancy, France

Introduction and objectives:

Since 2004, with the creation of the first recorded *High Entropy Alloy* (HEA) by simultaneously Cantor *et al.* [1] and Yeh *et al.* [2], numerous studies have shown the potential of such alloys, from nuclear applications to high ductility in cryogenic conditions. In this study, the objective is to manufacture new HEAs which would include light and refractory elements in order to bring high resilience and ultimate tensile strength to industrial components, while keeping a low density.

Ideally, the HEA should not exhibit intermetallic precipitates due to their brittle behavior, however, despite containing a low fraction of refractories, the HEAs still exhibited intermetallic phases, leading to the need for a model predicting the creation of intermetallics in HEAs.

Basics of HEAs: An HEA, as the name suggests, must possess a fundamental parameter to be labelled as such a high entropy of mixing $\Delta S_{mix} = -R \sum_i c_i \ln c_i$ and must be equal to at least $13.38 J. (mol. K)^{-1}$ (Figure 1), which is the result for a quinary, equimolar alloy.

Core properties of HEAs: According to Yeh *et al.*, giving an alloy such a high entropy of mixing would yield three effects:

A distorted lattice, a sluggish diffusion, a « cocktail effect » depicting the hardship of foreseeing the phases and properties of HEAs.

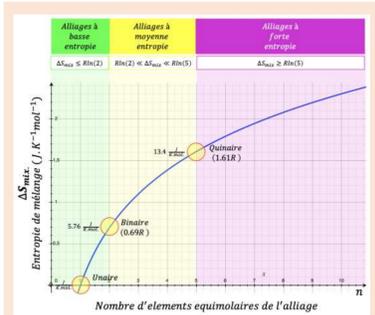


Figure 1: Evolution of the entropy versus the number of metallic elements.

Thermodynamic (Ω), steric (δr), electronic ($[VEC]$, $\delta\chi$) and chemical ($PSFE$) parameters of the HEA alloys [3-5]:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \text{ with: } \begin{cases} \Delta H_{mix} = \sum_{i=1, i \neq j}^n 4\Delta H_{i,j}^{mix} c_i c_j = \text{Enthalpy of mixing} \\ T_m = \sum_{i=1}^n c_i (T_m)_i = \text{Averaged melting temperature} \\ \Delta S_{mix} = -R \sum_{i=1}^n c_i \ln(c_i) = \text{Entropy of mixing (Fig1a)} \end{cases}$$

$$\delta r = \sqrt{\sum_{i=1}^n c_i (1 - r_i / \bar{r})^2}$$

Lattice distortion

$$\delta\chi_A = \sqrt{\sum_{i=1}^n c_i (1 - \chi_i / \bar{\chi})^2}$$

Allen's Electronegativity

$$[VEC] = \sum_{i=1}^n c_i [VEC]_i$$

Valence Electron Concentration

$$PSFE = 2p$$

(p = atomic % of [A] σ -forming elements)
Paired Sigma Forming Elements

c_i, r_i, χ_i and $[VEC]_i$ = Composition, Atomic size, Electronegativity and Valence Electron Concentration of the i^{th} element, respectively.
 \bar{r} and $\bar{\chi}$ are Average atomic radius and electronegativity of the HEA elements, respectively.

Criteria predicting the microstructure of the HEA Alloys [3-5] based on: $\Omega, \delta r, [VEC], \delta\chi$ and $PSFE$ parameters:

- ❖ Solid solution (SS): $-20 kJ.mol^{-1} \leq \Delta H_{mix} < 5 kJ.mol^{-1}$ and $\delta r < 6.2 \%$.
- ❖ Solid solution (SS only): $-5 kJ.mol^{-1} \leq \Delta H_{mix} < 5 kJ.mol^{-1}$ $\delta r < 3 \%$.
- ❖ Solid solution (only): $\Omega \geq 1.1$ and $\delta r \leq 6.6 \%$.
- ❖ Intermetallic phases (IP): $\Delta H_{mix} > 5 kJ.mol^{-1}$ and $\delta r > 3 \%$.
- ❖ (SS) + (IP) (or only IP): $1.1 \leq \Delta H_{mix} \leq 10 kJ.mol^{-1}$ and $\delta r > 3.8 \%$.
- ❖ (IP) (only): $\Delta H_{mix} > 20 kJ.mol^{-1}$.
- ❖ No (IP): $\Omega \gg 10$ and $\delta r < 3.8 \%$.
- ❖ VEC : (IP) if: $6.88 < [VEC] < 7.84$; (SS) if ($[VEC] > / < 6.88$).
- ❖ PSFE: For σ -phase: $[\sigma] = [A]_p [B]_q$; A $\in [VB - VIB]$ groups: $PSFE = 2p/2q [p \text{ at. } \%]$,
Frank - Kasper σ -phase and Laves - phase will form respectively with high probability if:
(σ -phase): $6.88 < [VEC] < 7.84$ and $PSFE > 40 \text{ at. } \%$ || (Laves - phase): $\delta r > 5.0 \%$ and $\Delta\chi_A > 7.0 \%$.

Material and procedures: Two alloys (refractory and light weight HEA, labelled RHEA-1 and LWHEA-1, respectively) were manufactured using high purity (> 99.95 wt.%) metallic flakes or powders (in which case they were pressed in pelleted form), arc-melted in Arc Furnace, in Argon atmosphere, and re-melted at least 5 times to ensure homogeneity. The two High Entropy Alloys, RHEA - 1 and LWHEA - 1 were substantially analyzed via XRD, ultra nano-indentation, SEM/EDS and TEM techniques.

Results and discussion (RHEA - 1 and LWHEA - 1 Alloys):

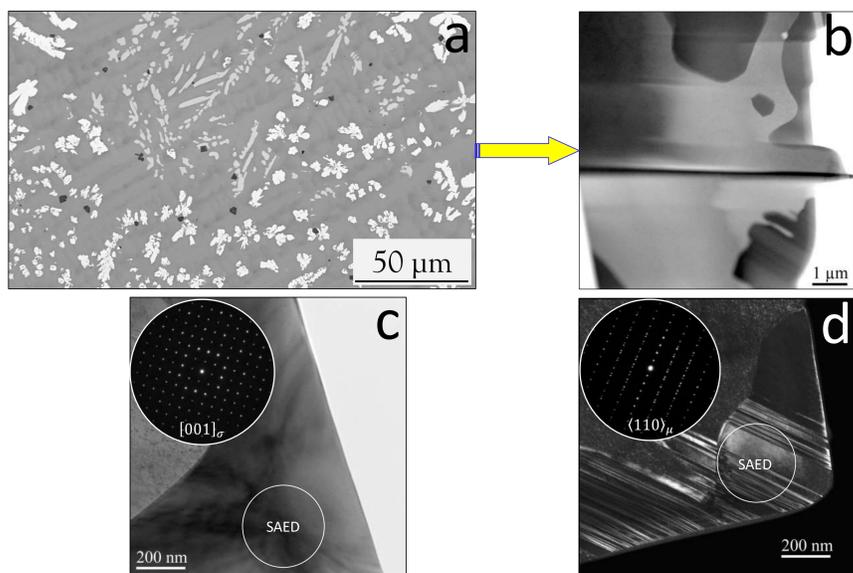


Figure 2: a) $(Cr_{24}W_7)(Mn_{21}Co_{24}Ni_{24})$ - (RHEA - 1): BSE-SEM image of the alloy: Clearer dendrites indicate their rich composition in heavy elements.

b) STEM-BF image of the sample showing the matrix and two minor intermetallic phases (IP): the Frank and Kasper phases: σ and μ -phases.

c) TEM image and associated Selected Area of Diffraction (SAED) along the $[001]$ of the σ -phase (ϵ to $P42/mnm$ with $a_\sigma = 8.8 \text{ \AA}$ and $c_\sigma = 4.5 \text{ \AA}$).

d) Dark-field TEM image and associated SAED pattern of the μ -phase (ϵ to $R\bar{3}m$ with $a = 4.72 \text{ \AA}$), recorded along $\langle 110 \rangle$.

The straight and brighter lines correspond to twins as established by electron diffraction characterisation, inserted SAED pattern in Figure 2d.

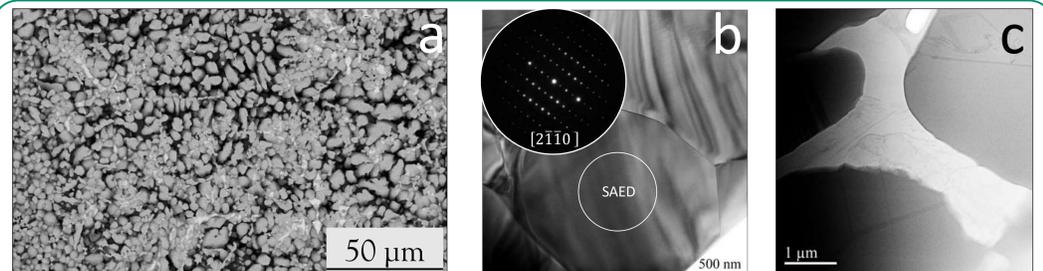


Figure 3: a) $(V, Al)_{20}(Ti, Ni, Ta)_{20}$ (LWHEA - 1) BSE-SEM image of the sample showing zones with clear and dark contrasts. Clearer contrast indicate that observed area is rich in heavy elements. b) BF-TEM image and the associated SAED pattern recorded along $[2\bar{1}\bar{1}0]$ of the C14 -Laves Phase (ϵ to $P6_3/mmc$ with $a_{C14} = 4.5 \text{ \AA}$ and $c_{C14} = 7.1 \text{ \AA}$).

c) STEM-BF image showing dislocations and planar defects in different Laves phase grains.

(at. %)	T_m	ΔS_{mix}	ΔH_{mix}	Ω	δr	$\delta\chi$	[VEC]	PSFE
RHEA - 1	1940 (K)	12.82 $J(mol.K)^{-1}$	-4.6 $kJ.mol^{-1}$	5.4 (-)	3.72 (-)	1.76 (-)	7.89 (-)	62 (%)
LWHEA - 1	2015 (K)	13.38 $J(mol.K)^{-1}$	-27.36 $kJ.mol^{-1}$	0.99 (-)	5.98 (-)	1.65 (-)	5.4 (-)	80 (%)

Conclusion and discussion : Bringing in HEA selection:

- RHEA - 1:** $\left\{ \begin{array}{l} \Omega = 5.4 \text{ and } \delta = 3.72\%: \text{Solid solution (SS) predicted and found,} \\ [VEC] = 7.89; PSFE: 48\%: \sigma \text{ predicted (IP) and found.} \end{array} \right.$
- LWHEA - 1:** $\left\{ \begin{array}{l} \Omega = 0.99 \text{ and } \delta = 5.98\%: \text{Solid solution (SS) not predicted,} \\ \Delta\chi_A = 19.3\% \text{ and } \delta = 5.98\%: \text{Laves phase (IP) predicted.} \end{array} \right.$

Empirical criteria are useful in HEA design but not conclusive when phases are in competition.

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