Phase prediction, microstructure and high hardness of novel light-weight high entropy alloys

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1. Introduction

HEAs have become a new research focus in the materials community in the last 14 years. The number of publications on this topic has grown enormously since the first publications in 2004 [1,2]. HEAs contains several major elements without a clear base element in contrast to conventional metallic alloys. The idea behind this new concept is that it is possible to stabilize a single phase solid solution (SS) by reducing Gibbs free energy, avoiding the formation of fragile intermetallic compounds (IC). Thus, the alloys are composed of five or more metallic elements in equimolar or nearly equimolar concentrations. HEAs have much higher mixing entropy values than traditional alloys in the liquid state or in the random SS state. Usually four “core effects” are used to describe the exceptional properties of HEAs: high entropy, sluggish diffusion, severe lattice distortion and cocktail effect [3]. Recently, a certain attention has been shifted to the study of multiphase HEAs with non-equatomic compositions due to their excellent properties [4–11]. Multiphase HEAs are mainly composed of two phases, which are known as Complex Concentrated Alloys (CCAs). The term HEAs remained for the sake of simplicity and will be used throughout the present work. The vast range of complex compositions, microstructures and the properties of these novel alloys were reviewed by Miracle et al. [12] and Zhang et al. [13].

Considering that the total number of possible HEAs is around $10^{177}$ [14], the implementation of an efficient method for predicting phase formation in HEAs is critical...
for the development of new engineering materials. Three
types of methodologies have been developed for predicting
phase formation in HEAs. At the beginning, various empir-
iclal thermo-physical parameters were proposed following
the Hume–Rothery rules [15–18]. Gao et al. reviewed these
parameters concluding that they are efficient in separat-
ing single-phase SS from amorphous alloys, but they fail to
separate single-phase SS from multiphase microstructures
[19]. More recently, the first-principles density functional
theory (DFT) calculations combined with hybrid Monte
Carlo/Molecular Dynamics (MC/MD) simulations have been
applied to HEAs with reasonably success [20,21]. To date,
the CALPHAD method can be regarded as the most robust
method for HEAs design [22]. This method can accelerate
the development of new HEAs through phase diagrams and
phase stabilities calculated from multicomponent thermody-
namic databases [23]. Most thermodynamic databases have
been developed for specific commercial alloys, which mean
that they usually have optimal compositional ranges of appli-
cation. But HEAs are not based on a main element like
traditional alloys. Therefore, some specific databases were
developed for phase prediction in HEAs. This databases are
TCHEA [24,25] and PanHEA [19,26] supplied by Thermo-CalTM
and PandatTM respectively, but they are mainly restricted to
transition metals containing HEAs. Thus, the latest version
of TCHEA has been developed in a 26 element framework
assessed to their full range of composition [27]. On the
other hand, PanHEA database is actually restricted to 10 ele-
ments [28]. In some cases, the use of standard databases for
commercial alloys such as TCAL and TCNI has shown
acceptable efficacy in predicting phase stability of HEAs
[29,30].

LWHEAs have recently attracted more attention for their
excellent mechanical properties [31–35] and the possibility
of reducing the weight in the transport or energy industry. In
this work, only HEAs with a density equal to or less than com-
tritional Ti alloys were defined as LWHEAs. Ti alloys are the heaviest
of the light alloys used in engineering to reduce the weight of structures and components [36]. The pioneering LWHEA
was nanocrystalline Al$_2$O$_3$Mg$_2$Sc$_3$Ti$_2$O$_7$ alloy, high hardness
(591HV) and low density (2.7 g/cm$^3$) were reported by Youssef
et al. [27]. To date, the hardness and hardness to density ratio
of Al$_2$Be$_2$Fe$_2$Si$_2$Ti$_2$ alloy are the highest reported before
[38]. The estimated strength of this alloy is 2976 MPa, which is
superior to those of traditional light-weight structural mate-
rials. Therefore, LWHEAs can be used as protective coating of
machine components and tools because of their high hardness
and excellent wear resistance [39].

Motivated by the above concerns, low-density and afford-
able Al$_5$Co$_3$Cr$_2$Fe$_2$Si$_2$, Al$_5$Co$_3$Cr$_2$Si$_2$Mn$_3$Ti$_5$ and
Al$_5$Co$_3$Cu$_2$Fe$_2$Cr$_2$Mn$_3$Ni$_3$Mg$_3$ alloys were designed by CAL-
PHAD method with the objective of achieving multiphase
microstructure to exceed the hardness, wearbehavior, and the
performance of low-density alloys in high-temperature appli-
cations. The major driver of the alloy design was to reduce
the density through increasing the molar % of Al, obtaining
Al-based non-equimolar HEAs. This has allowed the good liq-
uidity and castability of the molten alloys. Furthermore, the
addition of Cr was critically necessary for the formation of
high-temperature phases, while additions of Mn, Ni, Cu, Si
and Fe enhanced solid solution strengthening. To reduce the
alloy cost, expensive or scarce elements were avoided.

2. Experimental procedures

Thermo-Calc software (v. 2017b, Thermo-Calc Software AB,
Stockholm, Sweden) [40] in conjunction with thermodynamic
data TCAL5 was used for the equilibrium phases as a func-
tion of temperature calculation.

The raw elements with a minimum purity of 99.5 wt. %
were melted and merged in an alumina crucible in an electric
vacuum induction furnace model VIM (CONARC, Rancocas,
USA). Due to the high melting point of chromium, tablets of
Al-Cr containing 75 wt. % of Cr were used. Before melting, a
minimum chamber vacuum of 0.071 mbar was achieved and a
protective Ar gas atmosphere was introduced to prevent ox-
idation reactions during melting, with a chamber pressure of
400 mbar. The molten alloy was poured and solidified into a
metal die inside the furnace for at least 4 h.

Specimens of approximately 80 mm (length) × 80 mm
(width) × 140 mm (thickness) were obtained from the as-cast material. The samples of each alloy were cut from the ingots
and prepared according to standard metallographic proce-
dures by hot mounting in conductive resin, grinding, and
polishing.

The X-ray diffraction (XRD) equipment used to character-
ize the crystal structures of the alloys was a model DB ADVANCE
(BRUKER, Karlsruhe, Germany), with Cu Kα radiation, operated
at 40 kV and 30 mA. The diffraction diagrams were measured
at the diffraction angle 2θ range from 10° to 90° with a step
size of 0.01°, and 1.8 s/step. The powder diffraction file (PDF)
database 2008 was applied for phase identification.

The microstructure, the different regions and the averaged
overall chemical composition of each sample were investi-
gated using a scanning electron microscope (SEM), equipped
with an energy dispersive X-ray spectrometry (EDS) model
JSM-5910LV (JEOL, Croissy-sur-Seine, France).

Vickers microhardness FM-700 model (FUTURE-TECH, Kawasaki, Japan) was performed on the polished sample sur-
face using a 0.1 kg load, applied for 10 s. At least 10 random
individual measurements were made. Finally, density mea-
surement was conducted using the Archimedes method.

3. Results and discussion

The thermodynamic calculations of equilibrium phases in
manufactured alloys as a function of temperature were calcu-
lated using Thermo-Calc software and TCAL5 database as
shown in Fig. 1. TCAL5 database is commonly used for Al com-
comercial alloys. But according to previous works [30,31], the use
of this database in Al-based HEAs shows good agreement with
the experimental results. Regarding the very low cooling rate
used in the present study, it is reasonable to assume that the
alloys are close to thermodynamic equilibrium. Nevertheless,
it should be noted that calculations were made for homoge-

Please cite this article in press as: Sanchez JM, et al. Phase prediction, microstructure and high hardness of novel light-weight high entropy
Fig. 1 – Calculated phase diagrams of the manufactured alloys (a) $\text{Al}_{40}\text{Cu}_{15}\text{Cr}_{15}\text{Fe}_{15}\text{Si}_{15}$, (b) $\text{Al}_{65}\text{Cu}_{5}\text{Cr}_{5}\text{Si}_{15}\text{Mn}_{5}\text{Ti}_{5}$ and (c) $\text{Al}_{60}\text{Cu}_{10}\text{Fe}_{10}\text{Cr}_{5}\text{Mn}_{5}\text{Ni}_{5}\text{Mg}_{5}$; using Thermo-Calc software with TCAL5 database.

Fig. 1(a) shows that no major change is expected below 246 °C in $\text{Al}_{40}\text{Cu}_{15}\text{Cr}_{15}\text{Fe}_{15}\text{Si}_{15}$ cast alloy, which is the temperature of precipitation of the $\text{Al}\text{FeSi}(\gamma_1)$ phase. The $\gamma_1$ phase is predicted to slightly grow at the expense of BCC (B2) phase. The simulation suggested the formation of five phases at room temperature (RT), but the amount of $\text{Al}_3\text{Zr}_{5}(\text{D8m})$ is insignificant. The solidus temperature is 800 °C. In Fig. 1(b), five phases were predicted in equilibrium at RT for $\text{Al}_{65}\text{Cu}_{5}\text{Cr}_{5}\text{Si}_{15}\text{Mn}_{5}\text{Ti}_{5}$ cast alloy. All the phases are stable below 429 °C, and the solidus temperature is 534 °C. According to the Thermo-Calc equilibrium phase diagram of $\text{Al}_{60}\text{Cu}_{10}\text{Fe}_{10}\text{Cr}_{5}\text{Mn}_{5}\text{Ni}_{5}\text{Mg}_{5}$ cast alloy in Fig. 1(c), some qualitative and quantitative changes are expected below 326 °C in $\text{Al}_8\text{Mn}_5$ and $\gamma_1$-$\text{AlFeSi}$ phase. The solidus temperature is 506 °C. The whole quantity of these minor phases only represents 10 mol % of the amount of phase at RT. The diagrams suggest high phase stability of the designed alloys at high temperatures.

In Table 1, the thermodynamic calculations of equilibrium phases were summarized with the detailed description of their phase constitution and the amount of phase. The phase constitution obtained by TCAL5 database reflects that multiple elements can be dissolved in the sublattices. The amount of each element calculated for each sublattice has been neglected, this analysis has only been considered in a qualitative and not a quantitative way. Although the alloys are close to thermodynamic equilibrium, they are not expected to be in complete equilibrium. In addition, is supposed that the above mentioned high entropy, sluggish diffusion and severe lattice distortion effects can enrich the solution of the elements in each phase.
According to Thermo-Calc simulations, a multiphase character can be expected for the manufactured alloys, which is proven by the results of XRD measurements shown in Fig. 2. Considering that the intensities of the diffraction peaks of ordered phases are stronger than those of SS phases, the volume fractions of non-stoichiometric compounds appear to be significant for the manufactured alloys, which is in accordance. In HEA1, the experimental volume fraction of the phases is consistent with thermodynamic calculations of FeSi and γ-AlFeSi phases in Table 1. But the phase volume of Al13Fe5 calculated by XRD is quite higher. In HEA2, the predicted volume of phase and the experimental result obtained by XRD are in good accordance. In HEA3, fewer phases than those calculated by Thermo-Calc were observed in the XRD patterns. Thus, the volume fractions are slightly different. Experimental data suggest that Al13Ni2 is the main phase in the microstructure, in contrast to the amount of phase obtained by Thermo-Calc in Table 1. The major crystallographic data is summarized in Table 2.

The overall bulk composition of the alloys was estimated using EDS on large areas. At least three random measurements were made and the overall values are presented in Table 3. Overall values of Al80Cu15Fe5Cr5Si5 alloy, slightly deviate from the nominal concentration due evaporation losses of Mg during the melting process. Fig. 3(a) shows the SEM micrograph of the polished surface of as-cast Al80Cu15Fe5Cr5Si5 alloy. In Fig (b) the marked surface was magnified to identify small region marked as oxides, this region cannot be observed in Fig. 3(a) due to the negligible amount of phase that it represents in the alloy. The main areas in the morphology of the alloy are Region 1 and Region 2 (dark compounds). Surrounded by these regions, it can be observed Region 3 and a small amount of oxides.

In Fig. 4(a) qualitative elemental mapping was conducted by EDS to identify the distribution of elements in the observed regions. The results agree well with Fig. 3 and three areas can be distinguished in the elemental mapping. The main areas in the morphology of the alloy are Region 1, which is rich in Al-Cr and Region 2, rich in Al-Fe. Surrounded by these regions, it can be observed (Al,Cu)-rich area (Region 3) and small amount of oxides. From the EDS pattern in Fig. 4(b), it can be observed that the XRD pattern of the as-cast Al80Cu15Fe5Cr5Si5Mn5Ni5Mg5 alloy is shown in Fig. 2(c). Strong diffraction peak is observed at 44°, corresponding to Al13Ni2 and Al13Cu4Ni phases. The last phase was indexed as cubic MgCu4Al, phase, which was correlated to Mg2CuAl. The volume fractions of constitutive phases were calculated experimentally by XRD and detailed in Table 2. In HEA1, the experimental volume fraction of the phases is consistent with thermodynamic calculations of FeSi and γ-AlFeSi phases in Table 1. But the phase volume of Al13Fe5 calculated by XRD is quite higher. In HEA2, the predicted volume of phase and the experimental result obtained by XRD are in good accordance. In HEA3, fewer phases than those calculated by Thermo-Calc were observed in the XRD patterns. Thus, the volume fractions are slightly different. Experimental data suggest that Al13Ni2 is the main phase in the microstructure, in contrast to the amount of phase obtained by Thermo-Calc in Table 1. The major crystallographic data is summarized in Table 2.

### Table 1 – Phases predicted, phase constitution and amount of phase (mol %) of Al80Cu15Fe5Cr5Si5 (HEA1), Al80Cu20Cr20Si5Mn5Ti5 (HEA2) and Al80Cu15Fe5Cr5Si5Mn5Ni5Mg5 (HEA3) cast alloys, using of Thermo-Calc software with TCA5 database.

<table>
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<th>Phase constitution</th>
<th>Mol %</th>
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<td>Al80Cu15Fe5</td>
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<td>16</td>
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<tr>
<td></td>
<td>Al13Fe5</td>
<td>(Al, Cu, Fe, Al)</td>
<td>43</td>
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<tr>
<td></td>
<td>Al13Cu4Ni</td>
<td>(Al, Cu, Fe, Al)</td>
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<td>(Al, Cu, Fe, Al)</td>
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<tr>
<td></td>
<td>FeSi</td>
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<td>FeSi</td>
<td>(FeSi)</td>
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<td>HEA2</td>
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![Fig. 2](image-url) - XRD diffraction patterns of the cast (a) Al80Cu15Fe5Cr5Si5, (b) Al80Cu15Fe5Cr5Si5Mn5 and (c) Al80Cu15Fe5Cr5Si5Mn5Ni5Mg5.
Table 2 – List of phases, volume fraction (mol %), Space Group and the lattice parameters of Al$_{40}$Cu$_{15}$Fe$_{15}$Cr$_{15}$Si$_{15}$ (HEA1), Al$_{65}$Cu$_{5}$Cr$_{5}$Si$_{15}$Mn$_{5}$Ti$_{5}$ (HEA2) and Al$_{60}$Cu$_{10}$Fe$_{10}$Cr$_{5}$Mn$_{5}$Ni$_{5}$Mg$_{5}$ (HEA3) cast alloys obtained by XRD.

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<th>Alloy</th>
<th>Phase</th>
<th>Space Group</th>
<th>Volume fraction (mol %)</th>
<th>Lattice parameters (Å)</th>
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<td>Al$<em>{13}$Fe$</em>{5}$</td>
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<td>γ$_{1}$AlFeSi</td>
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<td>FeSi</td>
<td>P21 (198)</td>
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<td>Al$<em>{12}$Mn$</em>{12}$Si$_{12}$</td>
<td>Pm3 (200)</td>
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<td></td>
<td>Al$_{2}$Cu</td>
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<td>a = b = 4.22, c = 5.16</td>
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Table 3 – Chemical composition in at. % of the manufactured alloys.

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<th>Mn</th>
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<tr>
<td>Al$<em>{60}$Cu$</em>{10}$Fe$<em>{10}$Cr$</em>{5}$Mn$_{5}$</td>
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<td>7</td>
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<td>–</td>
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<tr>
<td>Al$<em>{60}$Cu$</em>{10}$Fe$<em>{10}$Cr$</em>{5}$Mn$<em>{5}$Ni$</em>{5}$Mg$_{5}$</td>
<td>60</td>
<td>11</td>
<td>10</td>
<td>6</td>
<td>5</td>
<td>–</td>
<td>5</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>

that the oxides region is mainly composed of impurities such as O, Mg and Sn.

Fig. 4(a) shows the complex morphology of Al$_{65}$Cu$_{5}$Cr$_{5}$Si$_{15}$Mn$_{5}$Ti$_{5}$ alloy, the microstructure is composed of four different regions. The contrast between regions is relatively high due to their complex compositions, which are composed of at least three elements. In Fig. 4(b), the marked surface was magnified for a better understanding of the complex morphology of the alloy. Elemental mapping was conducted by EDS as shown in Fig. 6 to identify the distribution of elements in the observed regions. The microstructure shows a matrix composed of Al-rich area (Region 1) and Al-Cu-rich area (Region 2). The brightest region is marked as Region 3, this region is composed

of Si and Ti. Finally, needle-like and irregularly sized Region 4 can be observed not homogeneously distributed throughout the whole alloy.

The SEM image in Fig. 7 of Al_{60}Cu_{10}Fe_{10}Cr_{5}Mn_{5}Ni_{5}Mg_{5} alloy shows a typical dendritic microstructure, indicating constitutional segregation during the non-equilibrium solidification. In contrast to Thermo-Calc predictions but accordingly with XRD results, only three regions can be distinguished. Fine cracks are also observed in Fig. 7(a).

In Fig. 8, elemental mapping was conducted by EDS to identify the distribution of elements in the observed regions. The dendrites (Region 1) as well as the interdendritic area (Region 2) consist of a mixture of all the elements in the alloy except Mg. The amount of Ni in the interdendritic region is significantly higher than in the dendritic region. There is compositional segregation inside the interdendritic region of Mg and Cu, marked as Region 3. As can be seen in Fig. 7(a), the main region of the alloy is Region 2. From elemental composition obtained in Fig. 8 and the phase constitution predicted in Table 1, Al_{14}Ni_{3} phase (Table 2) was correlated to the dendritic region. Moreover, this shows good agreement with the volumetric fraction of phases obtained experimentally in Table 2.

The microhardness of the fabricated alloys was evaluated on Vickers microhardness tester. The mean microhardness values with the standard deviation are 916 ± 99 Hv for Al_{40}Cu_{15}Cr_{15}Fe_{15}Si_{15}, 889 ± 281 Hv for Al_{65}Cu_{5}Cr_{5}Si_{15}Mn_{5}Ti_{5} and 743 ± 95 for Al_{60}Cu_{10}Fe_{10}Cr_{5}Mn_{5}Ni_{5}Mg_{5} alloy. The standard deviation of the microhardness in Al_{60}Cu_{10}Cr_{5}Si_{15}Mn_{5}Ti_{5} is very large due to the complex morphology observed in Fig. 5. Table 4 lists the microhardness and density of manufactured alloys. J Mater Res Technol. 2018. https://doi.org/10.1016/j.jmrt.2018.06.010
The hardness of Al₆₀Cu₃₀Fe₁₀Mn₂N₁₀M₈₅ alloy is the highest value reported for a LWHEA. In addition, the hardness of Al₆₀Cu₃₀Fe₁₀Mn₂N₁₀M₈₅ alloys is considerably higher. According to the Tabor relation [42], the Vickers hardness divided by 3 should approximate the yield strength. Values estimated by this way are 2994 MPa for Al₆₀Cu₃₀Fe₁₀Mn₂N₁₀M₈₅, 916 MPa for Al₆₀Cu₃₀Fe₁₀Mn₂N₁₀M₈₅, and 225 MPa for Al₆₀Cu₃₀Fe₁₀Mn₂N₁₀M₈₅. These values are higher than tungsten high speed tool steels and to those of traditional structural materials.

4. Conclusions

In summary, three novel Al₆₀Cu₃₀Fe₁₀Mn₂N₁₀M₈₅, Al₆₀Cu₃₀Fe₁₀Mn₂N₁₀M₈₅ and Al₆₀Cu₃₀Fe₁₀Mn₂N₁₀M₈₅ LWHEAs were designed by Thermo-Calc in conjunction with TCA5 database and produced by large-scale vacuum die casting. In addition, low density and high hardness from 743 to 916 HV was reported for manufactured alloys.

The LWHEAs have been fabricated by large-scale vacuum die casting. Our results suggested that affordable LWHEAs with high hardness can be adapted to large-scale industrial production.

There are some discrepancies between the experimental results and Thermo-Calc calculations. CALPHAD thermo-dynamic modeling successfully predicted the constituent phases, which are consistent with the experimental results. However, more phases are predicted by Thermo-Calc in Al₆₀Cu₃₀Cr₁₀Fe₁₀Si₁₅ and Al₆₀Cu₃₀Fe₁₀Cr₁₀M₈₅ alloys at RT than those observed in the samples. This suggests that despite having a slow cooling rate of solidification, total equilibrium state is not achieved in the manufacturing of the alloys. In general, this database has proven to be a good method for designing Al-based HEAs.

The high microhardness of the manufactured alloys is due to the presence of complex precipitates containing multiple elements on their respective sublattices as strengtheners.

New LWHEAs can provide a combination of low density and microstructures that could increase wear, strength, and performance at high temperatures of traditional light-weight alloys. The hardness of Al₆₀Cu₃₀Cr₁₀Fe₁₀Si₁₅ and hardness to density ratio of Al₆₀Cu₃₀Cr₁₀Si₁₅ are the highest of all LWHEAs previously reported. Therefore, we estimate...
that these newly designed LWHEAs have wide application prospects and can be of interest for future research. In addition to the applications mentioned above, we propose these alloys to be used as casing or structural materials of laptops or smartphones. For this, low density materials with high strength and especially high hardness are required to avoid scratches and protect the electronics.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgments

This work has been partially funded by the Basque government through the project Elkartek: KK-2017/00007.

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