Structural transformations of heat treated Co-less high entropy alloys

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Abstract. Co is considered to be one of the main ingredients in superalloys. Co is considered a critical element and its substitution is difficult due to its unique ability to form high temperature stable structures with high mechanical and corrosion/oxidation resistance. High entropy alloys (HEA) represent a relatively new concept in material design. HEA are characterised by a high number of alloying elements, in unusually high proportion. Due to their specific particularities, high entropy alloys tend to form predominant solid solution structures that develop potentially high chemical, physical and mechanical properties. Present paper is studying Co-less high entropy alloys with high potential in severe environment applications. The high entropy alloys based on Al-Cr-Fe-Mn-Ni system were prepared by induction melting and casting under protective atmosphere. The as-cast specimens were heat treated at various temperatures to determine the structure and property behaviour. Samples taken before and after heat treatment were investigated for chemical, physical, structural and mechanical characteristics. Sigma phase composition and heat treatment parameters had major influence over the resulted alloy structure and properties.

1. Introduction

High entropy alloys (HEA) are multicomponent alloys composed of five or more elements in equal or near equal proportions. Due to the Boltzmann’s hypothesis, where the maximum entropy of mixing of an alloy is obtained at equiatomic compositions, HEAs are expected to form only simple solid solution structures and develop superior mechanical and corrosion properties [1].

There is a substantial amount of papers that describe the thermodynamic intricacies related to solid solution formation in high entropy alloys. Significant criteria were developed based on the entropy, enthalpy, atomic size difference, valence electron configuration and electronegativity of various high entropy alloy systems [2-4], which are contributing to the selection of viable alloy compositions for different applications. Computer-Aided Phase Prediction in high entropy alloys was also performed on
various HEA systems, using specialized methods such as Calphad, Dendity Functional Theory, Monte Carlo or Molecular Dynamics, with significant results in approximating phase constitution and evolution at different compositions and temperatures [5-10].

Experimental trials were performed by various authors for a large number of alloy compositions containing mostly transitional elements (Co, Cr, Fe, Cu, Ni, Ti, Zr, etc.) with controlled additions of Al, Si, B or C for property enhancement[11-13]. Among all the Al-Co-Cr-Fe-Ni is the most studied system [14-16]. Co as a Face Centered Cubic (FCC) forming element was shown to produce stable solid solution structures with high mechanical and corrosion properties. Co was also seen to enhance mechanical resistance and hardness of HEA after annealing at up to 600°C. Nevertheless Co is a well-known critical element and its replacement is desirable in future industrial materials.

High entropy alloys based on Al-Cr-Fe-Mn-Ni system was shown to have interesting properties, especially after heat treatment at 800°C [17]. Aluminum was used to tailor the FCC to BCC transition in the newly developed alloy. Hardness values of up to 900Hv were obtained for the heat treated alloys.

Present paper is studying several high entropy alloys without Co content, based on Al-Cr-Fe-Mn-Ni system, taking into account variable solidification rates and heat treatment temperatures. A correlation of criteria, experimental and modelling results was performed on selected alloys.

2. Experimental

High entropy alloys based on Al-Cr-Fe-Mn-Ni system were prepared in an induction furnace type Linn MFG – 30 with inert atmosphere. Technical purity (99.9%) elemental Al, Cr, Fe, Mn and Ni were used as raw materials. A 500g charge of each alloy composition was initially loaded and melted under argon atmosphere, in a zirconia based crucible. The alloy was re-melted to ensure a uniform chemical composition and was cast at different solidification rates in graphite, steel and copper molds. The as-cast alloys were annealed in an electrical furnace, LHT 04/17 Nabertherm GMBH under protective atmosphere (Ar). The heat treatment stage was conducted at temperatures between 500 and 1100°C for 50 hours, with slow furnace cooling. Samples were taken before and after the heat treatment process for chemical, structural and mechanical analyses.

The chemical composition of the alloy was determined by optical emission spectrometry in inductively coupled (ICP-OES) using an Agilent 725 spectrometer. Optical microscopy investigation was performed with a Zeiss Axio Scope A1m Imager microscope. Samples were previously etched in an HCl-HNO3-CH3COOH-H2O solution to enhance the visibility of the grains and the grain boundaries. The morphology of the alloy was analysed by scanning electron microscopy (SEM) using a FEI Quanta 3D FEG operating at 20-30 kV, equipped with an energy dispersive X-ray spectrometer (EDS). The phase structure was analysed by X-ray diffractometry (XRD). Data acquisition was performed on BRUKER D8 ADVANCE diffractometer, using Bruker@DIFFRAC plus software, Bragg-Brentano diffraction method, Θ - Θ coupled in vertical configuration, with the following parameters: CuKa radiation, 2Θ Region: 20 ÷ 1240, 2Θ Step: 0.020, Time/step: 8.7 sec/step. Vickers microhardness of the samples was measured at room temperature using an optical microscope attachment (Anton Paar MHT10), with an applied load of 2N and slope of 0.6 N/s. In order to determine the average hardness of the alloy, seven indentations were performed on the surface of the as-cast and heat treated samples.

3. Results and discussion

3.1. Criteria calculations

The criteria for phase formation in high entropy alloys have been intensely studied in the past few years by various researchers [2-4,13,18-26]. Based on the definition of HEA concept, the alloys with mixing entropy (ΔSmix ) higher than the intermetallic compound formation entropy(ΔSInt ) can form mainly solid solution structures. Later, the mixing entropy was found to be defined mostly by the configurational entropy (ΔSconf ) [13], that needed to be higher than 11 J/moleK and lower than 19.5
Taking into account the definition of Gibb's free energy, in order to arrive to a stable alloy configuration is necessary to have a balanced contribution between configuration entropy and mixing enthalpy of the system ($\Delta H_{mix}$). Solid solution formation was also studied based on Hume-Rothery rule, where the atomic-size difference ($\delta$), electronegativity ($\Delta \chi$) and valence electron concentration (VEC) play an important role in alloy selection [20,21]. A $\Delta H_{mix} - \delta$ criterion was established [18, 19], where an enthalpy of mixing between -11.6 kJ/mol and 3.2 kJ/mol, and an atomic size difference smaller than 6.6% would define a system containing mainly solid solution structures. In order to take in consideration the entropy effect, an $\Omega$ factor was defined as the ratio between $\Delta S_{mix}$ and $\Delta H_{mix}$, and is considered only together with $\delta$. Thus if $\Omega > 1.1$ and $\delta < 3.6\%$ only solid solutions are formed, if $1.1 < \Omega < 10$ and $3.6\% < \delta < 6.6\%$ solid solutions and intermetallic compounds are formed, and if $\Omega > 10$ only solid solutions are formed [22]. The electronegativity (Allen) effect was also considered and values between 3% and 6% showed potential for the formation of solid solutions in multicomponent alloys [23]. The type of solid solutions formed in high entropy alloys was determined based on the valence electron concentration (VEC), where values smaller than 6.87 indicated the formation of only Body Centered Cubic (BCC) solid solutions, values between 6.87 and 8 showed that Body Centered Cubic (BCC) and Face Centered Cubic (FCC) structures coexist, and if VEC > 8 only Face Centered Cubic (FCC) structures were formed [24].

Due to the contradicting results obtained through the experimental process the criteria was further developed by other authors taking into consideration the effect of intermetallic phases formation more than solid solution stability criteria. Thus it was determined that a content larger than 40 at.\% of paired sigma-forming element (PSFE) is decisive on the formation of sigma phase in high entropy alloys [25,26]. If 25 at. \%< PSFE < 40 at.\% sigma phase may not exist and if PSFE < 20 at\% sigma phase should not be present in the alloy structure. The influence of intermetallic phases was also studied by other authors [3,4] that determined a $k_{1}^{cr}$ correlation factor ($k_{1}^{cr} = 1 - \frac{T \Delta \delta_{mix}}{\Delta H_{mix}} (1 - k_{2}) > \frac{\Delta H_{IM}}{\Delta H_{mix}}$) that needs to be higher than the ratio between intermetallic and solid solutions mixing enthalpies, in order to form only solid solutions. The calculation of criteria values for some alloy compositions derived from Al-Cr-Fe-Mn-Ni system are presented in table 1.

### Table 1. Criteria calculations for HEA structure prediction

| Alloy             | $\Delta S_{conf}$ J/molK | $\Delta H_{mix}$ kJ/mol | $\delta$ % | VEC | $\Delta \chi$ % | $\Omega$ | PSFE | $\Delta H_{IM}$ kJ/mol | $k_{1}^{cr}$ | $\Delta H_{IM}/\Delta H_{mix}$ |
|-------------------|--------------------------|-------------------------|-----------|-----|----------------|--------|------|------------------------|-------------|--------------------------|
| AlCrFeMnNi        | 13.38                    | -12.48                  | 5.82      | 7   | 5.6           | 1.74   | 40   | -27.84                 | 1.5         | 2.23                     |
| Al$_{0.5}$CrFeMnNi$_{0.5}$ | 12.96                  | -8.25                   | 5.28      | 7   | 4.95          | 2.66   | 50   | -19                    | 1.73        | 2.3                      |
| Al$_{0.5}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{0.5}$ | 12.51                  | -6.52                   | 5.00      | 7   | 4.85          | 3.36   | 60   | -15.52                 | 1.9         | 2.38                     |
| Al$_{0.5}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{1.5}$ | 12.61                  | -6.97                   | 4.72      | 7.16| 5.21          | 3.22   | 50   | -15.4                  | 1.85        | 2.2                      |
| Al$_{0.5}$CrFeMnNi$_{1.5}$ | 12.32                  | -5.5                    | 4.70      | 7.26| 4.6           | 3.9    | 47   | -13.42                 | 2.05        | 2.43                     |
| Al$_{0.5}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{1.5}$ | 12.16                  | -4.94                   | 4.53      | 7.12| 4.71          | 4.39   | 63   | -12.25                 | 2.15        | 2.48                     |

The results showed that most of the alloy compositions are characterized by the high entropy effect, with $\Delta S_{conf}$ and $\Delta H_{mix}$ close to the minimum interval limits, atomic size difference and electronegativity in required range and $\Omega$ showing a predominant formation of solid solution phases. BCC and FCC type of solid solutions are expected to form. The intermetallic formation criteria is confirming the previous findings with PSFE greater than 45 and $\Delta H_{IM}/\Delta H_{mix} > k_{1}^{cr}$ for most of the alloys. None of the alloy compositions are predicted to form only solid solution structures.

### 3.2. Experimental results

Three selected compositions, from Al-Cr-Fe-Mn-Ni system, are presented here in as-cast and heat treated state. The alloys presented a homogenous composition over the entire body of the resulted ingots (table 2).
Table 2. The alloys chemical composition.

| Alloy                  | Composition , wt. % |
|------------------------|---------------------|
|                        | Al   | Cr   | Fe   | Mn  | Ni  |
| Al_{0.5}Cr_{1.5}Fe_{1.5}Mn_{0.5} | 5.41 | 24.9 | 33.4 | 23.2 | 12.8 |
| Al_{0.5}Cr_{2}Fe_{1.5}MnNi | 3.82 | 30.6 | 27.3 | 18.2 | 19.8 |
| Al_{0.5}Cr_{1.5}Fe_{1.5}Mn_{0.5} | 3.15 | 30.7 | 33.6 | 20.3 | 12.2 |

Optical microscopy results (figure 1) for the as-cast alloys showed a predominant dendritic structure with larger amount of hard compounds in the Al_{0.5}Cr_{1.5}Fe_{1.5}Mn_{0.5} alloy, local interdendritic elemental segregations for the Al_{0.5}Cr_{2}Fe_{1.5}MnNi alloy and the presence of distinct rounded phases in the Al_{0.5}Cr_{1.5}Fe_{1.5}Mn_{0.5} alloy. Higher magnification, by SEM analyses (figure 2), revealed small and evenly distributed precipitated phases all across the alloys structure. The precipitates are larger and have different shapes in the Al_{0.5}Cr_{2}Fe_{1.5}MnNi alloy. XRD analyses (figure 3) revealed only BCC phases in Al_{0.5}Cr_{1.5}Fe_{1.5}Mn_{0.5} alloy (A2 and B2 types). The Al_{0.5}Cr_{2}Fe_{1.5}MnNi alloy showed a more complex structure with predominant BCC phases (A2 and B2 types) and minor FCC phase (A1 type). A significant proportion of sigma phase (20%) together with a BCC-A2 type phase was detected in the Al_{0.3}Cr_{1.5}Fe_{1.5}Mn_{0.5} alloy.

Figure 1. Optical micrographs of as-cast Al_{0.5}Cr_{1.5}Fe_{1.5}Mn_{0.5}, Al_{0.5}Cr_{2}Fe_{1.5}MnNi and Al_{0.3}Cr_{1.5}Fe_{1.5}Mn_{0.5} alloys.

Figure 2. SEM image of as-cast Al_{0.5}Cr_{1.5}Fe_{1.5}Mn_{0.5}, Al_{0.5}Cr_{2}Fe_{1.5}MnNi and Al_{0.3}Cr_{1.5}Fe_{1.5}Mn_{0.5} alloys.
Figure 3. X-ray diffraction pattern and phases for the as-cast alloys

The structural behavior of Al$_{0.3}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{0.5}$ alloy was studied at different solidification rates. Optical analyses (figure 4) of the structure revealed a smaller amount of hard phases in the interdendritic area and larger light colour interdendritic phases with the increase in the solidification rate. No significant changes were shown for the dendrite configuration.

Figure 4. Optical micrographs of as-cast Al$_{0.3}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{0.5}$ at low, medium and high solidification rates.

Figure 5. SEM images of heat treated Al$_{0.3}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{0.5}$ at 700, 800 and 900 °C
In figure 5 are presented SEM images of the heat treated alloys. The heat treatment process is shown to allow a substantial growth of the precipitates with the annealing temperature. The EDS mapping results (figure 6) show a significant Al and Ni density in the precipitates region that suggests the formation of NiAl-B2 type phase. X-ray diffraction analyses (figures 7-9) revealed important phase changes between different annealing states of the alloys. An BCC-B2 and sigma phase structure was seen for the Al$_{0.5}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{0.5}$, obtained by the annealing at 700°C or 800°C. By annealing at 900°C, the BCC-A2 phase became more stable. The Al$_{0.5}$Cr$_{2.5}$Fe$_{1.5}$MnNi alloy showed a structure formed of sigma phase and BCC-B2 at 700°C. At 800°C a FCC-A1 phase becomes stable. At 900°C a structure formed solely of BCC-A2 and FCC-A1 phases is revealed.

**Figure 6.** EDS mapping of Al$_{0.3}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{0.5}$ heat treated at 700°C

**Figure 7.** X-ray diffraction for Al$_{0.5}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{0.5}$ heat treated at 700, 800 and 900 °C
Figure 8. X-ray diffraction for Al$_{0.3}$Cr$_{1.3}$Fe$_{1.3}$MnNi heat treated at 700, 800 and 900 °C

Figure 9. X-ray diffraction for Al$_{0.3}$Cr$_{1.3}$Fe$_{1.3}$MnNi$_{0.5}$ heat treated at 700, 800 and 900 °C

The Al$_{0.3}$Cr$_{1.3}$Fe$_{1.3}$MnNi$_{0.5}$ showed a similar phase composition between the three annealing temperatures. The sigma phase, BCC-A2 and FCC-A1 phases were detected in all the annealed structures. As a conclusion, one can determine that BCC-A2 phase is more stable at higher temperatures, that BCC-B2 phase is mainly stable at lower temperatures and that the alloys with lower aluminium content are prone to form FCC type structures. From EDS and XRD analysis one can see that sigma phase is the matrix and NiAl is the precipitated phase.

The hardness tests results (figure 10) showed a large increase for the Al$_{0.3}$Cr$_{1.3}$Fe$_{1.3}$MnNi alloy, after heat treatment at 700, 800 and 900°C. The alloy hardness decreases strongly after an 1100°C heat treatment. Similar behaviour was indicated for the Al$_{0.3}$Cr$_{2}$Fe$_{1.5}$MnNi alloy, nevertheless hardness decreases at as-cast levels after the heat treatment at 900 °C. The Al$_{0.3}$Cr$_{1.3}$Fe$_{1.5}$MnNi$_{0.5}$ is showing no significant changes in hardness after the heat treatment process. By comparing the microhardness
values with the phase constitution one can observe some abnormal behavior of $\text{Al}_{0.3}\text{Cr}_{1.5}\text{Fe}_{1.5}\text{MnNi}_{0.5}$ that even if contains a good proportion of FCC-A1 phase has the highest value among all three alloys. In this case the hard sigma phase has the highest proportion and might as well influence strongly the alloy mechanical properties. Same can be said about the $\text{Al}_{0.5}\text{Cr}_{2}\text{Fe}_{1.5}\text{MnNi}$ alloy that provides a much higher hardness in the annealed structures with high sigma phase content. Nevertheless, sigma phase presence in the $\text{Al}_{0.5}\text{Cr}_{1.5}\text{Fe}_{1.5}\text{MnNi}_{0.5}$ annealed at 700ºC does not influence the microhardness value.

Microhardness measured for different solidification rates of $\text{Al}_{0.3}\text{Cr}_{1.5}\text{Fe}_{1.5}\text{MnNi}_{0.5}$ alloy (figure 11) does not indicate a significant variation, with a slightly higher value for the high rate solidification process.

![Microhardness variation with annealing temperature](image1)

**Figure 10.** Microhardness variation with annealing temperature

![Microhardness function of solidification rate for Al$_{0.3}$Cr$_{1.5}$Fe$_{1.5}$MnNi$_{0.5}$ alloy](image2)

**Figure 11.** Microhardness function of solidification rate for $\text{Al}_{0.3}\text{Cr}_{1.5}\text{Fe}_{1.5}\text{MnNi}_{0.5}$ alloy

3.3. Modelling results
Phase evolution and solidification of $\text{Al}_{0.5}\text{Cr}_{1.5}\text{Fe}_{1.5}\text{MnNi}_{0.5}$, $\text{Al}_{0.3}\text{Cr}_{2}\text{Fe}_{1.5}\text{MnNi}$ and $\text{Al}_{0.3}\text{Cr}_{1.5}\text{Fe}_{1.5}\text{MnNi}_{0.5}$ alloys were modelled with MatCalc software. MatCalc (The Materials Calculator) is a software toolbox for computational materials engineering that uses CALPHAD approach and covers the areas of multi-component phase equilibrium and thermodynamics as well as multi-phase precipitation kinetics and microstructure evolution in solid-state systems. Ni superalloy database was used for the present modelling goal. Nevertheless, the related diffusion database is not yet conclusive enough to be used in the precipitation and heat treatment calculations for high entropy alloys. Trials in this direction did not offer trusted results that could be used in our investigation.

The thermodynamic evaluation (figures 12-14) showed that all the alloys have a similar phase constitution based on sigma phase, BCC-B2 (NiAl), BCC-A2 and FCC-A1 types. The $\text{Al}_{0.5}\text{Cr}_{1.5}\text{Fe}_{1.5}\text{MnNi}_{0.5}$ has a smaller melting temperature than the other alloys, even if Al is in higher proportion. $\text{Al}_{0.3}\text{Cr}_{1.5}\text{Fe}_{1.5}\text{MnNi}_{0.5}$ alloy has a smaller FCC-A1 phase fraction than the other alloys, and
in the Al_{0.5}Cr_{2}Fe_{1.5}MnNi alloy remains stable until 1000ºC. The sigma phase is found to be dominant in the Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5} alloy. The NiAl-B2 phase is found in similar proportion in all the alloys. The solidification behaviour, determined by Scheil-Gulliver method, is also similar for all the alloys.

**Figure 12.** Phase equilibrium and solidification of Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5} alloy

**Figure 13.** Phase equilibrium and solidification of Al_{0.5}Cr_{2}Fe_{1.5}MnNi alloy

**Figure 14.** Phase equilibrium and solidification of Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5} alloy.

**Table 3.** Phases found through the experimental and modelling approaches.

| Alloy          | as-cast | 700ºC | heat treated | 900ºC | modelling         |
|----------------|---------|-------|--------------|-------|-------------------|
|                |         |       | 800ºC        |       |                   |
| Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5} | BCC-A2  | σ phase | BCC-A2       | BCC-A2 | σ phase           |
|                | BCC-B2  | BCC-B2 | BCC-B2       | BCC-B2 | BCC-B2(NiAl)     |
| Al_{0.5}Cr_{2}Fe_{1.5}MnNi     | BCC-A2  | σ phase | σ phase      | σ phase | σ phase           |
|                | BCC-B2  | BCC-B2 | FCC-A1       | FCC-A1 | BCC-B2(NiAl)     |
| Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5} | BCC-A2  | σ phase | σ phase      | σ phase | σ phase           |
|                | FCC-A1  | FCC-A1 | FCC-A1       | FCC-A1 | BCC-B2(NiAl)     |
Calculateds for phase stability at room temperature revealed structures formed of major sigma phase with minor B2-NiAl and BCC-A2 phases, for all the alloys. The sigma phase was determined to have molar fractions of: 0.59 for Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5} alloy, 0.66 for Al_{0.5}Cr_{2}Fe_{1.5}MnNi alloy and 0.7 for Al_{0.3}Cr_{1.5}Fe_{1.5}MnNi_{0.5} alloy.

Table 3 contains the phases found in the modelling results and experimentally in all the alloys at as-cast and annealed states, in proportional order. The correlation of empirical and modelling results showed significant differences. In the as-cast state only the Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5} presented sigma phase and in low proportion. The Al_{0.5}Cr_{2}Fe_{1.5}MnNi alloy contains a low proportion of FCC-A1 phase that was not predicted by the model. The annealing results enhanced sigma phase stabilisation in all the alloys. Still FCC-A1 phase is present in the Al_{0.3}Cr_{1.5}Fe_{1.5}MnNi_{0.5} similar to the findings of other authors [17].

One has to take into account that in conventional alloys the annealed state at slow cooling rates shows similar phases in the as-cast state, which is not the case in present HEA. Longer annealing holding times (longer than 50 hours) or much slower solidification rates obtained by controlled casting techniques could provide more accurate results.

The criteria for the prediction of solid solution formation in high entropy alloys were partially validated by the experimental trials and proved conclusive in relation to the modelling results.

4. Conclusions
Selected Co-less high entropy alloy compositions from the Al-Cr-Fe-Mn-Ni system were studied to determine structural behaviour in as-cast and annealed state.

Criteria calculation for several alloy compositions predicted formation of mixed solid solution phases (BCC and FCC) and intermetallic structures.

Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5}, Al_{0.5}Cr_{2}Fe_{1.5}MnNi and Al_{0.3}Cr_{1.5}Fe_{1.5}MnNi_{0.5} alloys were further prepared by induction melting and annealed at various temperatures.

Optical microscopy revealed similar dendritic structures with an additional phase distinguished in the Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5} alloy. Higher magnifications provided by SEM analyses revealed a uniform distribution of small precipitated phases. XRD determinations showed significant presence of BCC-A2 phase in all the alloys.

Lower solidification rates of the Al_{0.5}Cr_{1.5}Fe_{1.5}MnNi_{0.5} alloy, analysed at lower magnifications, determined a significant increase in the interdendritic phase and a decrease in the hard phase presence.

SEM-EDS analysis of the heat treated Al_{0.3}Cr_{1.5}Fe_{1.5}MnNi_{0.5} alloy showed similar uniform distribution of the precipitated phase but with larger precipitate sizes found in the samples heat treated at higher temperatures. Aluminum and nickel were found highly concentrated in the precipitated region.

Phase composition determined by x-ray analysis showed major sigma phase and BCC-B2 presence in all the alloys.

The microhardness values were strongly related to the proportion of sigma phase in the alloys, besides the Al_{0.3}Cr_{1.5}Fe_{1.5}MnNi_{0.5} sample heat treated at 700°C that presented unexpectedly low value.

Thermodynamic modelling of the selected high entropy alloys performed by the MatCalc software revealed suggestive results by predicting phase evolution for the specific compositions on a large temperature range, from 400°C to 1500°C. The study of alloys solidification by Scheil-Gulliver method was also provided. Precipitation and heat treatment results are not yet available for the selected high entropy alloys due to the lack in diffusion database research.

The correlation of experimental and modelling results revealed significant differences. Sigma phase was predicted by the modelling software as the main phase to form in all the alloys at room temperature, but was less found in the as-cast structures and not as predominant in the heat treated structures.

The initial theoretical criteria for phase prediction was entirely validated by the modelling method and partially validated by the experimental findings.
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