Heat treatments` effects on the microstructure and mechanical properties of an equiatomic Al-Cr-Fe-Mn-Ni high entropy alloy

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Abstract

The microstructure and properties of an equiatomic AlCrFeMnNi high entropy alloys (HEA) in the as-cast and heat treated conditions are presented. Using a variety of advanced characterization methods, it is shown that the AlCrFeMnNi solidified dendritically with Cr, Fe and Mn rich dendrite cores (DC) and Al and Ni rich interdendritic (ID) regions. Upon cooling, during solidification, AlCrFeMnNi alloy underwent spinodal decomposition. The DC area decomposed to a mixture of B2 and FCC matrix with nano cuboid BCC precipitates, while the ID region decomposed to a BCC matrix with B2 precipitates. The combination of relatively soft DC surrounded by hard ID regions resulted in high compressive strength combined with large compressive ductility and can be regarded as a “macro” composite material. The cracks initiate and propagate in the harder and more brittle ID regions. Heat treatments increased the amount of the FCC phase and enhanced microstructural coarsening. The undesirable σ phase was not detected after any heat treatment.

1. Introduction

High Entropy Alloys (HEA), also known as multi-principal element alloys or compositionally complex concentrated alloys, frequently comprise of simple solid solutions (FCC, BCC and HCP) instead of complex intermetallic compounds and, in some cases, yield unique combinations of high strengths [1–4], superior resistance to thermal softening [4–6], outstanding resistance to wear [7–9] and corrosion [10,11]. These alloys have generated considerable interest in the materials science community due to their potential industrial applications as tools, molds, dies as well as mechanical and furnace parts [12–14]. Many of the HEAs of interest are easily produced using conventional casting equipment, i.e. arc melting and induction melting, making mass production a possibility [13]. Therefore, correlations between the processing parameters and mechanical properties are essential for future structural applications involving HEAs [15]. In this regard, numerous studies were performed on the influence of thermo-mechanical processes (for example: heavily cold rolling followed by annealing [16,17], friction stir-processing [18] and different manufacturing processes such as laser fabrication [19]) on the mechanical properties and the microstructure of HEAs [20–22]. One of the advantages of HEAs is the wide range of properties adjustable via variations in manufacturing methods [23–26] and/or composition [27].

These alloys might provide unusual combinations of strength and ductility which can be foreseen if the ratio between the FCC/BCC phases (of which these alloys are comprised) is controlled. In general, the hardness of the FCC phase is between 1.0 and 2.0 GPa [3]. HEAs having only the FCC phase (for example: CoCrCuFeNi) exhibit ductilities between 20 and 60%, and usually exhibit significant work hardening [28]. One way to improve the strength of these HEAs is by adding Al to the alloys. It was found, that additions of Al to CoCrCuFeNi results in hardness increase from 1.33 to 6.55 GPa [3], due to the formation of the harder BCC phase. With sufficient Al, the precipitation of nano-sized B2 precipitates also leads to increased hardness values. However, these alloys become more brittle and microcracks at the corners of microhardness indents are observed in some alloys [3]. Microstructure of alloys with relatively high Al contents ($x>1$) composed of a

BCC matrix with B2 precipitates, with hardness values varying typically between 5.00 and 6.00 GPa, while the ductility decreases to less than 5% [28]. Similar results were obtained in $\text{Al}_x\text{CoCrFeNi}$ [29,30] alloys (i.e. without Cu). The phase content of these alloys changes as a function of Al concentration and it can be summarized as follows. First, when x is less than 0.3 the alloy is 100% FCC. As the value of x is increased past 0.3, a BCC phase is observed. If the Al concentration is increased above 0.9, the alloy consists of the BCC phase only. The hardness of these alloys also changes accordingly from around 1.0 GPa to above 5.0 GPa.

It was reported that equiatomic CoCrFeMnNi HEA possesses single FCC solid solution which solidifies dendritically [12], exhibiting relatively low strength and large tensile strain [31,32]. In current research, it was decided to replace the Co in the CoCrFeMnNi by Al. There are several reasons for that: first, Co does not play a central role in promoting a BCC matrix or B2 precipitates [33] while Al, as it was mentioned earlier, is known to transform the soft FCC phase to the harder BCC phase in other HEA systems [29,34–36]. Second, maintaining Cr in the alloy was considered desirable since Cr is known as a BCC stabilizer and for its impact on prompting passivity and improving oxidation resistance. For example adding 6 at% Cr to $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{35}\text{Al}_{15}$ (at%) alloy induced the formation of protective oxide scales on the surface [37,38] and reduced susceptibility to H embrittlement [39]. Moreover, Cr lowers the yield strength and, therefore, contributes to the improved ductility, possibly by easing dislocation cross-slip in the deformed FCC phase where most of the Cr resides [37,38].

Following the logic of Al addition presented earlier, AlCrFeMnNi HEA seemed promising with regard to its potentially-desirable mechanical properties. Thus, the goals of the present work were to characterize the cast structure and to study the influence of different heat treatments on the microstructure and mechanical properties of the equiatomic AlCrFeMnNi alloy and to understand the impact of Co replacement by Al on the mechanical properties of the AlCrFeMnNi alloy.

2. Experimental procedures

2.1 Arc melting

A nominally equiatomic AlCrFeMnNi alloy was prepared by non-consumable electrode arc melting under a Ti-gettered, high-purity argon atmosphere on a water-cooled copper hearth. Approximately 50 grams of raw materials, with purities higher than 99.5%, were melted for ~30 s at least 5 times to ensure that all raw materials were well mixed in liquid prior to solidification. The buttons were flipped over between each melting cycle in order to improve chemical homogeneity. The nominal and actual compositions of the AlCrFeMnNi alloys are summarized in Table 1. The actual composition was checked using EDS in the SEM in at least 25 different locations and all fell within the measured compositions presented in Table 1. The dimensions of the button after melting were ~37 mm diameter and maximum height of ~13 mm. After arc melting, the buttons were cross-sectioned into 4 mm-wide strips. The middle of the 4 mm strips was sliced into rectangles with $4 \times 4 \text{ mm}^2$ cross-section and a height of 8 to 13 mm. Then, the height of the rectangles was

abraded from both sides to 6 mm as this was the desired length for compression tests. The rest of the specimens were used for microstructure and microhardness analyses.

The metallographic specimens were mounted in phenolic, abraded on SiC papers up to 4000 grit and then polished with the final polish on a Buehler Vibromet using 0.05 μm colloidal silica for 16 to 20 h. The colloidal silica is a slightly alkaline solution in these HE alloys. Therefore, no additional etchant was applied prior to examination by Field-Emission Scanning Electron Microscopy (FESEM) equipped with Energy Dispersive Spectroscopy (EDS) capabilities. For the EDS measurements, the raw intensity data were ZAF corrected to an accuracy of ± 0.4 at% for the elements studied [40].

2.2 Differential thermal analysis (DTA)

Differential thermal analysis (DTA) (DTA-NETZSCH Thermal Analysis DSC 404 cell) was conducted on small rectangular pieces that were cut to fit into the small alumina crucibles used for DTA. Each piece weighed between 130 to 170 mg. The scans were made from room temperature to 1500 $^{\circ}\text{C}$ at rates of 20 $^{\circ}\text{C}/\text{min}$. Each specimen was heated and cooled 3 times under essentially identical conditions.

2.3. Heat treatments

Based on the DTA results and taking into account information available on similar HEA systems the following heat treatments were performed: 400, 600, 850, 1040 and 1200 $^{\circ}\text{C}$ for 4h and water quenched. It turn out that [41] the 1100 $^{\circ}\text{C}$ temperature that was chosen by Kao *et al* [36] for homogenization of similar alloy is too low while 1200 $^{\circ}\text{C}$ (used here) is better for homogenization. Following Kao *et al* [36] and according to our experience, 4 h is sufficient for creating the majority of microstructural changes in the specimen. Heat treatments were performed in air. Up to 1040 $^{\circ}\text{C}$ the oxidation was minimal. The homogenization at 1200 $^{\circ}\text{C}$ was performed under Ar protective environment.

2.4 X-ray diffraction (XRD) analysis

XRD patterns of polished and unetched samples were recorded on a Rigaku RINT 2100 diffractometer with Cu K_{α} radiation ($\lambda = 0.15406$ nm). Data were acquired from 20 to 100 $^{\circ}$ 2θ with a step size of 0.02 $^{\circ}$ and step time of 15 s/step.

2.5 Transmission Electron Microscopy (TEM) analysis

For transmission electron microscopy (TEM), slices were cut from the as-cast or heat treated samples and abraded to a thickness of about 150 μm , from which 3 mm diameter disks were drilled out with an abrasive hole saw that utilizes fine SiC particles. Final thinning was performed in a Fischione twin-jet electropolisher using a solution of 10% HClO_4 + 90% CH_3OH at approximately -30 $^{\circ}\text{C}$. When necessary, a Gatan Duo-Mill argon ion mill was used to further thin the specimens using 5 KV Ar ions at an angle of 5 $^{\circ}$ for 0.5 to 2 h.

2.6. Compressive tests

For compressive testing, the rectangular specimen dimensions were $4 \times 4 \text{ mm}^2$ in cross section and 6 mm in height. The long dimension was perpendicular to the bottom of the ingot. The samples were compressed using a strain rate of $5 \times 10^{-3} \text{ mm/s}$. At least three different specimens were tested.

3. Results

3.1 Differential thermal analysis (DTA) results

DTA scans for the AlCrFeMnNi alloy are shown in Figure 1. Three thermal cycles were performed and exhibited essentially identical results. Consequently, only the third cycle data are shown in Figure 1. For clarity, the derivative curves that were used to determine the inflection points and the corresponding peak temperatures, are not shown here. As can be seen, the cooling curve for the AlCrFeMnNi alloy contains only two exothermic peaks at 1300 and 1345°C. Lower temperature peaks corresponding to solid-state reactions were not observed. The cooling peak at 1345°C corresponds to the start of solidification whereas the larger 1300°C peak corresponds to the liquidus temperature of the AlCrFeMnNi alloy.

3.2 X-ray diffraction (XRD) results

XRD patterns from the AlCrFeMnNi alloy in the as-cast condition and after different heat treatments are presented in Fig. 2. It can be seen that the as-cast alloy is BCC with a small extra peak near 30° corresponding to the (001) reflection of the ordered BCC (i.e. B2) phase. After heat treatments above 400°C an additional peak was observed and was assigned to the FCC phase. The FCC and BCC peaks are shifting slightly to the left with increasing heat treatment temperature. It is possible that during the heat treatments there are compositional changes which affect the lattice parameter.

3.3 Microstructural examination

3.3.1 SEM examination

Backscattered electron images (BEI) of the AlCrFeMnNi alloy in the as-cast condition indicate that the microstructure consists of grains, columnar at the cast bottom (Fig. 3a) and equiaxed grains at the cast top (Fig. 3b), with dendritic sub-structure composed of a dendrite core (DC) and interdendritic regions (ID). The compositions of the different regions and the phases were measured using EDS in the SEM and the results are summarized in Table 2. The DC microstructure consisted of a matrix rich with Cr+Fe+Mn with cuboid Al+Ni rich precipitates, see Fig. 3c and Table 2. The ID regions are rich with Al+Ni (around 45.6 at.%) . The microstructure consisted of an Ni+Al rich matrix with precipitates, this morphology has been reported to form by spinodal decomposition [29,42] (see Fig. 3d).

The microstructures of the AlCrFeMnNi alloy after the 4h heat treatments at 400, 600, 850, 1040 and 1200°C are shown in Figure 4 and at higher magnification in Figure 5. It can be concluded that heating up to 850°C did not cause significant microstructural changes whereas heating at 1040°C resulted in significant microstructure coarsening and loss of the dendritic microstructure.

Heating to 1200°C caused further coarsening with the resulting high (bright) and low (gray) average atomic number (Z) regions. The dark cuboid phases in the DC regions (Fig. 3c) lose their facets and become spherical. In addition small bright precipitates in the gray phase could be observed after the heat treatment at 1200°C (Fig. 5f). The average compositions of the DC and ID regions in the as cast condition and as a function of heat treatment temperature from 400-850°C (Table 3) did not change significantly due to the heat treatments. The compositions of the different phases in AlCrFeMnNi alloy after the 4h heat treatment at 1040 and 1200°C are summarized in Table 4.

3.3.1) TEM examination

High Angle Annular Dark Field (HAADF) and EDS X-ray maps of the different elements in the as-cast AlCrFeMnNi alloy are presented in Fig. 6 and in the ID region at higher magnification in Fig. 7. As can be seen in figures 6 and 7, the Ni and Al segregate to the lower Z phase whereas Fe, Cr and Mn partition to the higher Z phase.

The internal microstructure of the DC and ID regions are presented in Bright-field (BF) and Dark-field (DF) TEM images with their corresponding selected area diffraction (SAD) patterns in Figures 8 and 9, respectively. A BF TEM image (Fig. 8a) and two DF images (Figs. 8b and 8c), taken from the reflections $(220)_{\text{FCC}}$ and $(111)_{\text{B2}}$, suggest that the DC matrix composed of a mixture of B2 and FCC phases with BCC precipitates as seen in the SAD insert in Fig 8a. In contrast, the ID regions (Fig. 9) are composed of a BCC matrix and B2 precipitates, as seen in the SAD insert in Fig 12a.

3.4 Mechanical properties

The results of the microhardness measurements of AlCrFeMnNi alloy in the as-cast condition and after different isochronal heat treatments (Table 6) revealed that the hardness of the alloy increases from 4.42 to 4.85 GPa after heating at 400°C and then decreases monotonically to 4.0 GPa after heating at 850 and 1040°C. In contrast, after heating at 1200°C the hardness increases again to 5.0 GPa.

When performing measurements with 100 g. the indentation is bigger than dimensions of the DC or ID regions. Therefore, it was impossible to measure the microhardness of the DC and ID alone.

The engineering compressive stress/strain curves for AlCrFeMnNi alloy in the as cast condition and after different heat treatments are given in Fig. 10 and the mechanical properties are summarized in Table 7. As can be seen from Table 7 and Fig. 10 the engineering compressive yield strength increases when heated to 400°C. Above 850°C the yield strength decreases as temperature increases. However, at 1200°C the yield strength increases again. The compression test result exhibits the same tendency as the micro-hardness results.

SEM images illustrating side branches of the main crack propagation for specimens compressed till fracture are given in Figure 11. As shown in the figure - cracks propagate solely in the ID regions or near the DC/ID interface regions. Heat treatments up to 850°C did not change the path of the crack propagation.

4. Discussion

During cooling, AlCrFeMnNi liquid started to solidify upon reaching the liquidus surface. As solidification proceeded, the liquid and solid followed their respective liquidus and solidus surfaces. Once solidification had completed, the macro-structure of the studied AlCrFeMnNi alloy consisted of Cr+Fe+Ni rich (around 64.5 at%) dendrite core (DC) and Ni+Al rich inter dendrite (ID) regions (see Table 2) resulting from the coring effects [43]. At the bottom of the cast, up to 3 to 4 mm from the copper chill, the heat flow is perpendicular to the cast bottom, therefore, columnar morphology was observed. At distances greater than 4 mm, the heat flow dissipates evenly imposing equiaxed morphology. In spite of this difference, the microstructure of these areas was similar, but coarser at the cast top due to lower cooling rates. Different composition of the DC and ID imposed different microstructure in these areas. The matrix of the DC region composed of a mixture of B2 and FCC phases with BCC cuboid precipitates (Fig. 8) therefore relatively soft. In the ID regions (Fig. 9), B2 particles with modulated basket-weave morphology are embedded in the BCC matrix (Figs. 3b and 9a) relatively hard and brittle. Although FCC peaks were not seen in the as-cast condition in the X ray diffractogram (Fig. 2), it might be undetectable due to this phase's low volume in the studied sample [46]. After the heat treatment, the volume fraction, as well as the size, of the FCC phase has increased and was clearly seen on the X- ray diffractogram (Fig. 2).

The microstructure of the B2 precipitates embedded in the BCC matrix (or vice versa) was reported for the AlCoCrFeNi HEAs and it was attributed to spinodal decomposition [41,44,45]. Therefore, we also believe that the microstructure of the AlCrFeMnNi alloy in both regions (DC and ID) is originated by spinodal decomposition process. Summarizing the results presented in current work, following solidification route can be proposed. Most probably, the first solid to solidify in both regions is a BCC saturated solid solution with different average compositions. During further cooling down the solid entered into the miscibility gap and decomposed by spinodal decomposition. Since the DC and ID have different average compositions it influenced the decomposition. The DC decomposed to a BCC solid solution matrix and cuboid BCC precipitates. Upon further cooling the BCC solid solution matrix underwent solid state reaction creating a mixture of FCC and B2 phases while the cuboid BCC precipitates remained unchanged. The ID region underwent spinodal decomposition to a BCC matrix and B2 precipitates. Thus, following reactions could be concluded:

DC region: BCC (SS) --> BCC (SS) + BCC (P) --> (B2+FCC (M)) + BCC (P)

ID region: BCC (SS) --> BCC (M) --> B2 (P)

Where SS stands for solid solution, P - precipitates and M - matrix.

After heat treatment above 400°C, FCC peak at around $2\theta=41^\circ$ became visible on X-ray diffractogram (Fig. 2). Despite the fact that in our research only bulk samples were studied and, thus, their XRD patterns might suffer from preferred orientation, we believe that peak height can be used here as an indication of the FCC quantities since all XRD specimens were cut in the same orientation with respect to the cast button. Therefore, it can be concluded that amount of the FCC phase was increased during the heat treatments.

Heat treatments caused mostly phase coarsening but did not change the existing phases after solidification as can be seen from the X-ray diffractograms presented in Fig. 2. Up to the heat treatment of 850°C no morphology change was observed (Figs. 4 and 5). It is possible that some phase coarsening occurred. In contrast, heat treatment at 1040°C caused more pronounced coarsening in both regions (DC and ID), while ID region underwent the most significant changes so that the dendritic nature almost vanished (Figs. 4e and 5e). After the heat treatment at 1200°C, ID regions reappear with different morphology, i.e. the ID regions decomposed to a dark and white small round precipitates (Figs. 4f and 5f). Some dissolution of the DC also occurred and round spheres with the same microstructure as in the ID appeared in the DC regions (Figs. 4f and 5f). This microstructure can be interpreted as a result of partial dissolution of phases existing in the alloys and formation of solid solution in those regions. Upon cooling to room temperature from 1200°C, the material reentered the miscibility gap and underwent, again, spinodal decomposition creating nanosize round precipitates. According to our results, we can propose that effective solution treatment of the AlCrFeMnNi alloys should be done at slightly higher than 1300°C temperature (see DTA results in Fig. 1), these results are similar to published for the AlCoCrFeNi HEA [41].

As it can be expected, these morphological changes have an impact on the mechanical properties (Fig. 10 and Tables 6 and 7). It was found that after heat treatment at 400°C the σ_y , σ_{UTS} and compression strain to fracture increased compared to the as cast state. Same trend was observed in the micro-hardness measurements, the values increased from around 4.42 to 4.85 GPa. Further heating up to 1040°C caused monotonic strength reduction of the compression mechanical properties (see Table 7) as well as microhardness reduction up to 4.00 GPa (Table 6). While after heating to 1200°C - the strength and microhardness increased to 5.0 GPa. These observations are consistent with the described earlier in this paper microstructural changes occurring in the alloy as a function of the heat treatments. The monotonic strength reduction up to 1040°C can be attributed to coarsening and the increase at 1200°C is probably due to the spinodal decomposition reaction which took place during cooling from this temperature. The cooling rates during quenching from 1200°C into water are much larger than the cooling rates during solidification resulting in finer B2 precipitates which induced higher microhardness.

Using compression test, individual properties of the ID and DC areas were evaluated. The cracks, initiated due to the compression test, propagated in the ID regions or near the interface between the DC and ID regions (Fig. 11) and usually terminated when the crack tip reached the DC region. Similar results were reported for the AlCoCrFeNi alloy [41]. The crack initiation and propagation in the DC regions in the AlCrFeMnNi alloy can be explained by the different hardness of these areas. Due to the small DC and ID dimensions only an averaged microhardness could be measured. Since the DC regions are composed of a matrix containing a mixture of soft FCC and B2 (along with cuboid BCC precipitates), we might speculate that the presence of a soft and ductile FCC phase in the DC regions makes this region more ductile than the ID regions. Therefore, the cracks propagated in the ID regions. Similar to the AlCoCrFeNi alloy [41], the

AlCrFeMnNi alloy might be considered as a “macro-” composite material, in which strength is attained by the strong and brittle ID regions and ductility is gained by the DC regions, which are relatively soft.

It is clear that mechanical properties of HEAs depend on the ratio of the FCC/BCC phases formed. Ren et al. [33] suggested that the forming ability of an FCC or BCC phases in HEAs can be estimated by means of the relationship between Ni_{eq} and Cr_{eq} , respectively, like the case in stainless steels. Where: $Ni_{eq} = Ni\% + 0.5Mn\% + 0.25Cu\%$ and $Cr_{eq} = Cr\% + Fe\%$. According to this criterion, Cr and Fe will promote the formation of BCC structure while Ni and Mn will promote the growth of the FCC phase. On the other hand, Ni is known as the strongest FCC stabilizer among all FCC stabilizers in HEAs. Increasing Ni:Al ratio has a tendency to form FCC phases [46]. The DC regions in the as cast AlCrFeMnNi alloy are richer in Mn (24.4 at.%, as compared to 19.7 at.% in the ID regions, see Table 2). Therefore, it is not surprising that the matrix in the DC regions comprised in our case of a mixture of B2 and FCC structures. In contrast, the ID regions contained larger amounts of Al which might enhance the formation of BCC and B2.

The valence electron concentration (VEC) criterion is another criterion for predicting the phases that will be formed in a HEAs, i.e. FCC or BCC. It was suggested by Guo *et al* in [47]. The VEC parameter is calculated according to the following equation:

$$VEC = \sum_{i=1}^n c_i (VEC)_i ,$$

where c_i , and $(VEC)_i$ are the atomic percentage and VEC for the i^{th} element, respectively.

They suggested that FCC phase will form when the $VEC \geq 8$ whereas BCC phase will be formed when $VEC < 6.87$. FCC and BCC mixture will coexist in between. The VEC for Ni and Co are 9 and 10, respectively, thus according to the VEC criterion they are FCC stabilizers, whereas Al and Ti have VEC of 3 and 4, respectively meaning - BCC stabilizers. Therefore, in our case taking out the, FCC stabilizer, Co from the CrCoFeMnNi alloy and replacing it with Al which is BCC stabilizer was justified. Instead of the soft and ductile CrCoFeMnNi ($\sigma_Y = 200$ MPa and over 50% uniform tensile strain obtained in tension tests) alloy [48] the AlCrFeMnNi alloy is hard (over 1200 MPa compression yield stress (Table 7)) but still maintaining relatively large compressive strain (12%). This unique combination was obtained due to the relatively soft DC which enhances the compressive strain while the hard ID gave the strength. In contrast, adding Al to the CrCoFeMnNi without taking out the Co would have increased drastically the strength but reduced the tensile strain to less than 5%[48]. Another justification for the addition of Al is its ability to prevent oxidation at elevated temperatures. It enabled to perform the heat treatments in air up to around 1040°C. The existence of Al in the alloy also prevents oxidation at elevated temperatures up to around 1040°C allowing in our research heat treatments in air. In addition, Cr, which is BCC stabilizer [33], lowers the yield strength and, therefore, contribute to the improved ductility, possibly by easing dislocation cross-slip in the deformed FCC phase where most of the Cr resides[37,38]. Li et. al. [49] suggested that large quantities of Al and Cr might be avoided for better ductility, in this way B2 structure, which is brittle, suppressed.

VEC criterion can be used not only for the BCC/FCC prediction. Tsai *et al* [50] suggested to use the VEC criteria to suppress the appearance of σ phase that might increase dramatically the hardness and reduce the tensile or compressive strain upon heat treatments between 500 to 1000°C. It was shown that when $VEC > 7.84$ σ phase will be suppressed. In our study no σ phase was detected in the as cast as well as after the heat treatments despite that VEC of the DC and ID regions of the studied here AlCrFeMnNi alloy are 6.8, and 7, respectively (based on the data presented in Ref [51]). This point needs to be further investigated.

5. Summary

The impact of heat treatments on the microstructure and mechanical properties of the equi-atomic AlCrFeMnNi alloy, prepared by non-consumable electrode arc melting, was investigated using SEM, TEM, XRD analyses and compressive and Vickers micro-hardness tests. The following results were obtained:

- 1) The AlCrFeMnNi alloy solidified dendritically with a Cr+Fe+Mn rich DC and Ni+Al rich ID regions. Both regions underwent spinodal decomposition upon cooling to room temperature. However, because of the different average composition, they decomposed differently. The DC region composed of a FCC+B2 mixture as matrix and nano cuboid BCC precipitates. The ID composed of BCC matrix and B2 precipitates.
- 2) Heat treatments coarsened these phases, as expected, but also increased the amount the FCC phase so that it became detectable by XRD analysis. Although in current study no σ phase was observed, VEC parameter indicated that σ phase should have been observed. This point needs to be further investigated.
- 3) Cracks initiated and propagated in hard ID regions or near the interface of the DC and ID regions. Usually, cracks terminated when their tip reached the DC region. It can be attributed to the presence of the soft and ductile FCC phase in the DC region, while the ID area comprised of the hard and brittle BCC and B2 phases.
- 4) The combination of a relatively soft DC and hard and brittle ID regions provided unique high compression strength combined with large contraction. Thus, the AlCrFeMnNi alloy can be regarded as a “macro” composite material.
- 5) We estimated that the homogenization temperature of the investigated HEA is close to 1300°C.

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Figure Captions

Fig. 1. Differential thermal analysis (DTA) curves for the 3rd cycle (heating and cooling as marked on the graphs) for the AlCrFeMnNi alloy.

Fig 2. XRD patterns from the AlCrFeMnNi alloy in the as-cast condition and after the different heat treatments .

Fig. 3. Backscattered electron images (BEI) of the AlCrFeMnNi alloy in the as-cast condition. a) Columnar dendrites at the bottom of the button where the grain boundary is marked GB. b) Equiaxed dendrites at the cast top. Numbers refer to points where composition was measured – see Table 2. c-d) Higher magnification images of the dendrite core-DC (c) and interdendritic-ID (d) regions.

Fig. 4. BEI of the AlCrFeMnNi alloy in the as-cast condition (a) and after 4h at the different temperatures: b) 400 °C, c) 600 °C, d) 850 °C, e) 1040°C and f) 1200 °C. Numbers refer to points where composition was measured – see Table 3.

Fig. 5. BEI of the AlCrFeMnNi alloy illustrating the microstructure after the different heat treatments at higher magnification: a) as-cast, b) 400 °C, c) 600 °C, d) 850 °C, e) 1040 °C and f) 1200 °C. Numbers refer to points where composition was measured and the squares are area counts— see Table 4.

Fig. 6. High angle annular dark field HAADF image and EDS maps of the different elements in the as-cast AlCrFeMnNi alloy.

Fig. 7. High angle annular dark field HAADF image and EDS maps of the different elements in the as-cast ID regions of AlCrFeMnNi alloy.

Fig. 8. TEM images illustrating the microstructure of the DC regions. (a) Bright field TEM image showing matrix and precipitates (about 200nm in size); b and c) dark field images taken from the reflections $(220)_{FCC}$ and $(111)_{B2}$, respectively; A selected area diffraction pattern taken from this area is shown in the inset in (a).

Fig. 9 . TEM images illustrating the microstructure of the ID regions. (a) Bright field TEM image showing matrix and precipitates (elongated $0.3 \times 1 \mu\text{m}$ in size); (b) dark field image taken from the reflection $(010)_{B2}$, lighting up the precipitates. A selected area diffraction pattern taken from this area is shown in the inset in (a).

Fig. 10. Engineering compressive stress/strain curves for AlCrFeMnNi alloy in the as-cast condition and after different heat treatments.

Fig. 11. BEI SEM images of the as cast AlCrFeMnNi alloy illustrating the sub crack propagation after the compression till fracture. .

Table 1. Nominal and measured compositions (in at. %) of the HEA used in this investigation.

Element	AlCrFeMnNi alloy	
	Nominal	Measured
Al	20	19.3
Cr	20	20.5
Fe	20	21.5
Mn	20	17.9
Ni	20	20.8

Table 2. Measured compositions (in at. %) of the dendrite core region, the dendrite periphery regions and the individual phases in the as-cast AlCrFeMnNi alloy. The numbers refer to Fig. 3.

Elements	Dendrite Cores (DC)			Dendrite Peripheries (ID)		
	Average	Precipitate*	Matrix*	Average	White phase*	Dark phase*
	Point 1	Point 3	Point 4	Point 2	Point 5	Point 6
Al	16.3	23.6	13.2	21.4	14.3	25.4
Cr	24.0	16.8	29.2	17.8	28.9	16.5
Fe	18.1	16.0	19.9	16.9	19.5	16.2
Mn	24.4	16.9	29.9	19.7	29.2	16.8
Ni	17.2	26.7	7.8	24.2	8.1	25.1

* Due to the small particle size, the EDS data is not accurate but does indicate trends in partitioning.

Table 3. EDS compositions (in at. %) for AlCrFeMnNi alloy after different heat treatments. The numbers refer to Fig. 4.

Elements	As-cast		400°C		600°C		850°C	
	DC	ID	DC	ID	DC	ID	DC	ID
	(point 1)	(point 2)	(point 3)	(point 4)	(point 5)	(point 6)	(point 7)	(point 8)
Al	16.3	21.4	16.9	20.3	16.5	21.3	16.2	20.7
Cr	24.0	17.8	23.5	18.1	23.8	17.3	24.1	17.9
Fe	18.1	16.9	18.5	17.5	18.4	17.7	18.0	17.6
Mn	24.4	19.7	23.8	19.6	24.4	19.6	24.6	19.7
Ni	17.2	24.2	17.3	24.5	16.9	24.1	17.1	24.1

Table 4. EDS results (in at. %) from the former dendrite cores and the interdendritic regions for AlCrFeMnNi alloy after heat treatment of 1040 and 1200 °C. The numbers refer to Fig. 5.

Elements	1040 °C			1200 °C					
	Point 1*	Point 2*	Point 3*	Area 4	Area 5	Point 6*	Point 7*	Point 8	Point 9*
Al	16.6	33.2	19.0	13.4	28.4	26.2	21.5	13.6	27.5
Cr	24.8	5.9	22.3	27.7	8.8	12.8	17.5	27.7	9.0
Fe	19.2	13.2	18.3	19.7	14.9	16.5	15.9	19.6	15.0
Mn	26.9	9.8	21.9	27.2	12.3	17.1	17.6	27.4	12.0
Ni	12.5	37.9	18.5	12.0	35.6	27.4	27.5	11.7	36.5

* Due to the small particle size, the EDS data is not accurate but does indicate trends in partitioning.

Table 6. Microhardness [in GPa] of the two alloys in the as-cast condition and after 4h at the different temperatures at load of 100 g.

As-cast	400°C	600°C	850°C	1040°C	1200°C
4.42±0.10	4.85±0.15	4.60±0.15	4.25±0.15	4.00±0.10	5.00±0.20

Table 7: Summary of engineering compressive yield stress, compressive maximum stress and compressive [strain](#) to fracture for AlCoCrCuFeNi alloy in the as cast condition and after different heat treatments.

State	Yield stress [MPa]	Maximum stress [MPa]	Compressive strain to fracture [%]
As cast	1370	1800	12
400°C	1600	2440	22
850°C	1500	2130	16
1040°C	1400	2000	18
1200°C	1490	2460	25