A novel medium entropy alloy based on iron-manganese-aluminum-nickel: influence of boron addition on phase formation, microstructure, and mechanical properties

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Abstract
A novel Medium Entropy Alloy (MEA) based on Fe–Mn–Al–Ni has been designed adopting High Entropy Alloys’ (HEAs) phase formation rules, and the effects of minor boron addition on phase content and mechanical properties have been separately investigated. Boron-free Fe_{(52.71-x)}Mn_{31.11}Al_{5.09}Ni_{11.08}B_x (x = 0, 0.05, 0.2, 0.5, 0.7 wt%) MEA showed a single face-centered cubic (FCC) structure. XRD results indicated that with 0.05 and 0.2 wt% boron addition the system maintains its single-phase structure. Further boron addition led to the formation of metal boride intermetallics by the volume fractions of 4.6 and 6.1% of Fe_2B intermetallic phase in as-cast and 2.7 and 5.4% in Deformed and Heat-treated (D&H) samples according to Rietveld analysis for 0.5 and 0.7 wt% boron doped alloys, respectively. Boron addition had a positive effect on grain size reduction of the system where just by 0.05 wt% boron addition the grain size has been almost halved compared to boron free as-cast sample. Moreover, it was observed that as the boron level increases, the hardness value increases. With in the all samples subjected to thermomechanical process, 0.7wt % boron doped alloy showed the best yield strength (increasing by ~50%, from 151 MPa to 222.5 MPa) and ultimate tensile strength (increasing by ~15%, from 476 MPa to 543 MPa) compared to undoped MEA at comparable ductility (ε > 60%).

1. Introduction

High-entropy alloys (HEAs) have become one of the most interesting research fields in materials science and engineering in the last decade. These alloys, which are also known as multi-principal element alloys (MPEAs), or complex concentrated alloys (CCAs), unlike conventional alloys, which contain one and rarely two base elements, are composed of multiple principal elements, with the possible number of high entropy compositions extending substantially more than conventional alloys. The advent of HEAs caused a paradigmatic shift in the design of modern alloys [1, 2]. Various studies have proved that HEAs possess high strength from their severe lattice distortion effects, and good high temperature creep and softening resistance properties from their sluggish diffusion effect [3–8]. In this study, benefiting from the phase formation rules of HEAs, which is summarised in table 1, a multi-principal element alloy based on iron (Fe), manganese (Mn), aluminum (Al) and nickel (Ni), with a single FCC phase has been designed.

The motivation in the development of this MEA can be described as follows: Firstly, Manganese and Nickel were selected as the FCC phase stabilizers. Secondly, Iron has been selected to reduce the cost. Thirdly, Aluminium is selected as the low-density element which can reduce the density of the alloy. In addition, elements used in this MEA have ideal atomic radiuses (i.e. there is no considerable difference in their atomic
Firstly, in order to determine the eligible compositions, the relevant thermodynamic parameters for 633 different compositions of (Fe,Mn,Al,Ni) system were calculated by using 5% increments of (q, v, w, y, z) values where 5 ≤ q, y, z, w ≤ 50.

Considering the values of mixing entropy as −15 < \( \Delta H_{mix} < +5 \) kJ mol\(^{-1}\), atomic size difference as \( \delta \leq 5.5\% \), \( \Omega \) parameter as \( \Omega > 1.5 \), theoretical density lower than 7.5 g cm\(^{-3}\) and calculated melting temperature higher than 1350 °C (providing an alloy with a lower density and higher melting point), ten compositions have emerged as eligible candidates for the (Fe,Mn,Al,Ni) alloying system. Table 3 shows the related thermodynamic calculation of these compositions in the order of lower to higher density.

Originally table 3 indicate that all calculated alloys are medium entropy alloys (MEAs) as the calculated configurational entropy values are; 0.69 R < SS\(_{ideal} < 1.61 R \) [11], but \( \Omega \) parameters with values greater than

radius) and as such, the alloy has the potential to be studied as a reasonable multi-component alloy. Regarding HEAs with FCC crystal structures, the preliminary mechanical tests indicate that this type of alloys possesses good ductility but poor strength [8]. To strengthen HEAs with FCC solid solution phase, plenty of investigations have been reported concerning to address the problem: solid solution strengthening [14–16], nitriding [17], deformation strengthening [7, 18] and annealing [19] are the methods have been used to strengthen this type of HEAs. In this study boron (B) as the minor alloying element has been selected due to following reasons; firstly, boron was nominated for its effective grain size reduction which was reported in various studies [20–26]. Secondly, the effects of thermomechanical treatments in the presence of boron were in a great deal of interest, and not last but least, the formation of possible M\(_2\)B as the probable phases according to Valence Electron Concentration (VEC); 

\[
\begin{align*}
\Delta H_{mix} &= \sum_{i=1}^{N} 4\Delta H_{mix}^{SS} c_i c_j \\
\Delta S_{mix} &= -R \sum_{i=1}^{N} c_i \ln c_i \\
\delta &= 100 \sqrt{\sum_{i=1}^{N} c_i^2 (1 - \frac{d_i}{r})^2} \\
\Omega &= \frac{T_0 \Delta S_{mix}}{\Delta H_{mix}} \\
T_m &= \sum_{i=1}^{N} c_i (T_m) \\
VEC &= \sum_{i=1}^{N} c_i (VEC)_i
\end{align*}
\]

### Table 1. Thermodynamic parameters related to phase formation of HEAs.

| Parameter | Note | References |
|-----------|------|------------|
| \( \Delta H_{mix} \) | \( \sum_{i=1}^{N} 4\Delta H_{mix}^{SS} c_i c_j \) | [9] |
| \( \Delta S_{mix} \) | \( -R \sum_{i=1}^{N} c_i \ln c_i \) | [11] |
| \( \delta \) | \( 100 \sqrt{\sum_{i=1}^{N} c_i^2 (1 - \frac{d_i}{r})^2} \) | [12] |
| \( \Omega \) | \( \frac{T_0 \Delta S_{mix}}{\Delta H_{mix}} \) | [2] |
| \( T_m \) | \( \sum_{i=1}^{N} c_i (T_m) \) | [9] |
| \( VEC \) | \( \sum_{i=1}^{N} c_i (VEC)_i \) | [13] |

1. The quantitative criterion of \( \Delta H_{mix} \) for the formation of simple solid solutions is: \( -15 < \Delta H_{mix} < 5 \) kJ mol\(^{-1}\).
2. The quantitative criterion of \( \Delta S_{mix} \) for the formation of simple solid solutions is: \( 12 \leq \Delta S_{mix} \leq 17.5 \) (J/K/mol).
3. Atomic size difference (\( \delta \)) parameter with a value lower than 6.6%, will enhance the chance of obtaining a single-phase solid solution structure.
4. As long as \( \Omega > 1.1 \), then the effect of the mixing entropy is greater than that of the enthalpy of mixing at the melting point, and the high-entropy phase(s) tends to form.

### Table 2. Physical properties of selected elements for the multi-principle alloying system.

| Property | Fe | Mn | Al | Ni | B |
|----------|----|----|----|----|---|
| Atomic Number | 26 | 25 | 13 | 28 | 5 |
| Molar Mass (g mol\(^{-1}\)) | 55.85 | 54.94 | 26.98 | 58.69 | 10.88 |
| Density (g cm\(^{-3}\)) | 7.87 | 7.47 | 2.70 | 8.90 | 2.30 |
| Atomic Radius (Å) | 1.241 | 1.350 | 1.432 | 1.243 | 0.880 |
| Melting Point (°C) | 1538 | 1244 | 660 | 1453 | 2300 |
| VEC | 5 | 7 | 3 | 10 | 3 |

2. Design and modelling

Firstly, in order to determine the eligible compositions, the relevant thermodynamic parameters for 633 different compositions of (Fe\(_q\),Mn\(_v\),Al\(_w\),Ni\(_z\)) system were calculated by using 5% increments of (q, v, w, y, z) values where 5 ≤ q, y, z, w ≤ 50.

Generally, is been calculated using Miedema Model [18].

\[
T_m = \frac{\sum_{i=1}^{N} c_i (T_m)}{\sum_{i=1}^{N} c_i}
\]

\[
\Omega = \frac{\frac{H_{mix}}{T_0 \Delta S_{mix}}}{\Delta H_{mix}}
\]

\[
\delta = 100 \sqrt{\sum_{i=1}^{N} c_i^2 (1 - \frac{d_i}{r})^2}
\]

\[
\Delta H_{mix} = \sum_{i=1}^{N} 4\Delta H_{mix}^{SS} c_i c_j
\]

\[
\Delta S_{mix} = -R \sum_{i=1}^{N} c_i \ln c_i
\]

\[
\Omega > 1.1
\]

\[
\delta < 6.6%
\]

\[
\Omega \leq 6.87 \text{ (FCC)}
\]

\[
\Omega > 6.87 \text{ (BCC + FCC)}
\]
1.1. ensure that the effect of the mixing entropy is greater than that of the enthalpy of mixing at the melting point, and the high-entropy phase can be formed. The values for enthalpy of mixing and $\delta$ parameter show that they are in good agreement with suggested value ranges for a HEA which is given in Table 1. Considering all the facts, Fe$_{50}$Mn$_{30}$Al$_{10}$Ni$_{10}$ MEA has been selected for further investigations as it possesses the lowest density compared to other MEAs. It is worthy to mention that, even though VEC value of almost all alloys suggests a mixed FCC and BCC phases during solidification since $6.87 \leq VEC \leq 8.0$, it gives no clue about the stability of these phases in different temperatures. To better understanding of phase content and stability of these phases, the pseudo-binary phase diagram of Fe$_{50}$Mn$_{30}$Al$_{20-x}$Ni$_{x}$ and property diagram of Fe$_{50}$Mn$_{30}$Al$_{10}$Ni$_{10}$ MEA has been prepared using the TCFE9 database of Thermo-Calc program (Figure 1).

Figure 1. (a) Pseudobinary phase diagram of Fe$_{50}$Mn$_{30}$Al$_{20-x}$Ni$_{x}$ MEA, (b) The property diagram of Fe$_{50}$Mn$_{30}$Al$_{10}$Ni$_{10}$ MEA.

Investigating the relevant phase and property diagrams demonstrates Fe$_{50}$Mn$_{30}$Al$_{10}$Ni$_{10}$ alloy with double phase structure. But a more thorough analysis related to solidification behavior of Fe$_{50}$Mn$_{30}$Al$_{10}$Ni$_{10}$ alloy shows that the BCC phase is stable down to \(\sim 1050 ^\circ C\) and after that all BCC structure will be totally replaced with FCC structure.

Establishing the Fe$_{50}$Mn$_{30}$Al$_{10}$Ni$_{10}$ MEA with a single FCC phase, the further calculation of boron addition to the mentioned MEA has been carried out. For this reason, it has been decided to study 0.05, 0.2, 0.5 and 0.7 (by wt%) boron addition to Fe$_{50}$Mn$_{30}$Al$_{10}$Ni$_{10}$ MEA. Table 4 shows weight percent equivalent for Fe$_{50}$Mn$_{30}$Al$_{10}$Ni$_{10}$ MEA regarded to weight percent addition of boron in upcoming sections.

To study the effects of boron addition on the phase formation of the mentioned alloying system, both computational and theoretical approaches have been carried out, which the results are shown in figure 2 and Table 5, respectively.

Although the computed phase diagram offers M$_2$B intermetallic phases for all boron-doped MEAs, it is worthy to mention that CALPHAD simulation neglects the critical boron solubility factor, which specifies about critical solubility level; below this critical level boron tends to prefer random high-angle grain boundaries upon

### Table 3. Thermodynamic calculations of eligible compositions based on defined parameters in the (Fe$_{x}$Mn$_{y}$Al$_{z}$Ni$_{w}$) alloying system.

| No | Fe (%) | Mn (%) | Al (%) | Ni (%) | $\Delta G_{\text{mix}}$ | $\Delta S_{\text{conf}}$ | $\Delta S_{\text{mix}}$ | $\Delta H_{\text{mix}}$ | $\%T_m$ | $\Omega$ | VEC | TD |
|----|--------|--------|--------|--------|----------------|----------------|----------------|----------------|--------|-----|-----|-----|
| 1  | 50     | 30     | 10     | 10     | -19.5849      | 1.1683         | 9.5028         | -6.72          | 5.1751 | 1354 | 1.91 | 7.4 | 7.319 |
| 2  | 50     | 5      | 15     | 30     | -22.015      | 1.1421         | 9.2900         | -9.51          | 5.4307 | 1366 | 1.33 | 7.8 | 7.376 |
| 3  | 50     | 25     | 10     | 15     | -20.6242     | 1.2080         | 9.8257         | -7.22          | 5.1518 | 1364 | 1.86 | 7.55 | 7.392 |
| 4  | 45     | 5      | 15     | 35     | -22.8425     | 1.1611         | 9.4446         | -9.98          | 5.4202 | 1362 | 1.29 | 7.9 | 7.429 |
| 5  | 45     | 25     | 10     | 20     | -21.8763     | 1.2580         | 10.2330        | -7.96          | 5.1377 | 1360 | 1.75 | 7.65 | 7.445 |
| 6  | 45     | 45     | 5      | 5      | -15.0673     | 1.0182         | 8.2823         | -3.82          | 4.6849 | 1358 | 2.94 | 7.4 | 7.462 |
| 7  | 50     | 20     | 10     | 20     | -21.2076     | 1.2206         | 9.9284         | -7.56          | 5.0958 | 1375 | 1.81 | 7.7 | 7.466 |
| 8  | 50     | 40     | 5      | 5      | -14.9865     | 1.0126         | 8.2370         | -3.68          | 4.7159 | 1373 | 3.07 | 7.45 | 7.482 |
| 9  | 40     | 5      | 15     | 40     | -23.3016     | 1.1674         | 9.4955         | -10.41         | 5.4097 | 1358 | 1.24 | 8 | 7.482 |
| 10 | 40     | 25     | 10     | 25     | -22.8843     | 1.2899         | 10.4922        | -8.66          | 5.1235 | 1356 | 1.64 | 7.75 | 7.498 |

*1.td: theoretical density.
moderate diffusion temperature. Beyond that, the formation of boride compounds could be seen as it leads to a decrease in the Gibbs free energy \[20, 28, 29\].

Referring to table 5 and thermodynamic calculations due to values of mixing enthalpy, \(\delta\) and \(\Omega\) parameter it can conclude that up to 0.2 wt% boron addition the formation of single-phase solid solution is possible, but by further boron addition (as in 0.5 wt% and 0.7 wt% boron doped alloys) and with \(\delta\) parameters higher than 6.6%, the formation of intermetallics such as \(\text{M}_2\text{B}\), in addition to solid solution phase(s) is highly probable. To sum up, combining extracted information from theoretical modeling with computational approach indicates that these medium entropy alloys correspond with phase formation rules of HEAs and high possibility to form single FCC solid solutions, while with the high amount of boron addition (0.5 and 0.7 wt%) formation of boride compounds can be inevitable.

### 3. Experimental procedure

The samples were prepared by vacuum arc melting and casting method. Elements of Fe, Mn, Al, Ni and B with purity higher than 99.9% were used as raw materials. The alloys were remelted for four times to ensure the homogeneity of MEAs. The metal molds of \(6.5 \times 20 \times 80\) mm were used to fabricate the plate-shaped samples. Hot-rolling, homogenizing, cold-rolling and annealing processes (as thermomechanical treatment procedure) were committed, respectively, to the as-cast samples. For hot rolling, the samples were subjected to \(1100^\circ\text{C}\) for 30 min followed by approximately 50% thickness reduction and air cooling (from 5.65 mm to 2.7 mm).

Homogenization process was carried out after hot rolling. Samples were homogenized at \(1000^\circ\text{C}\) for 45 min and then quenched in the water. Further grain refinement was achieved through cold-rolling to a thickness reduction ratio of 50% of homogenized samples (to 1.1 mm). For recrystallization of boron-doped and undoped alloys, the rolled sheets were annealed at a temperature of \(1000^\circ\text{C}\) for 30 min and subsequently quenched in water.

The crystal structure of the samples was characterized by an x-ray diffractometer (XRD Rigaku-MiniFlex 600), using Cu-K\(\alpha\) radiation scanning from \(30^\circ\) to \(90^\circ\) for as-cast and \(30^\circ\) to \(100^\circ\) for D&H samples, at a scanning rate of \(2^\circ/\text{min}\). Rietveld analysis carried out to the samples to calculate the phase amount of MEAs in multiphase structural alloys. Phase fractions were obtained by Rietveld analysis of XRD patterns using the Materials Analysis Using Diffraction (MAUD) program [30]. Microstructure characterization was performed with SEM (Scanning electron microscope) images of NOVA NANOSEM 650 device using a secondary electron detector. The tensile test of the D&H samples was measured with the optical extensometer using the Shimadzu Autograph AG-IS applying 250 kN and a deformation rate of \(1.0 \text{ mm min}^{-1}\). The Vicker Hardness Values of all
Table 5. Thermodynamic calculation of boron doped Fe<sub>50</sub>Mn<sub>30</sub>Al<sub>10</sub>Ni<sub>10</sub> MEAs.

| MEA            | ΔG<sub>mix</sub> (kJ mol<sup>-1</sup>) | ΔS<sub>conf</sub> (J/K.mol) | ΔS<sub>mix</sub> (J/K.mol) | ΔH<sub>mix</sub> (kJ mol<sup>-1</sup>) | δ (%) | T<sub>m</sub> (°C) | Ω    | VEC | TD (g cm<sup>-3</sup>) |
|----------------|--------------------------------------|-----------------------------|-----------------------------|---------------------------------------|-------|-------------------|------|-----|-------------------|
| 0.05 wt% Boron doped | -13.173                              | 1.1681R                     | 9.7116                      | -6.9339                               | 5.42  | 1356              | 1.90 | 7.39 | 7.3236            |
| 0.2 wt% Boron doped    | -13.231                              | 1.1675R                     | 9.7067                      | -7.5631                               | 6.06  | 1362              | 1.75 | 7.36 | 7.2864            |
| 0.5 wt% Boron doped    | -13.343                              | 1.1662R                     | 9.6957                      | -8.7706                               | 7.14  | 1375              | 1.52 | 7.29 | 7.2133            |
| 0.7 wt% Boron doped    | -13.414                              | 1.1652R                     | 9.6875                      | -9.3393                               | 7.76  | 1384              | 1.41 | 7.25 | 7.1656            |
prepared samples was measured by applying 50 grams of load on the Future-Tech FM-700 device for 10 s and for each sample, at least 10 hardness tests were performed to obtain sufficient statistics. To examine the validity of the theoretical density, the experimental density of the alloys has been calculated using Archimedes Principle. To calculate experimental density at least five measurements have been carried out for each sample and the average value has been taken as the experimental density.

### 4. Results

An MEA based on HEA principles has been designed and evaluated. The model proposes that benefiting from high entropy principles, by the enthalpy of mixing values in the range of $-15$ and $5 \text{ kJ mol}^{-1}$ and $\Omega$ parameters higher than 1.1, it is still possible to obtain a single-phase structure up to 6.6% atomic size difference ($\delta$ parameter). Even addition of minor alloying elements (Boron in this case) with a careful arrangement of enthalpy of mixing ($\Delta H_{\text{mix}}$), $\Omega$ parameter, and ($\delta$) parameter could lead to single solid solution phases.

The XRD patterns for Fe$_{52.71-x}$Mn$_{31.11}$Al$_{5.09}$Ni$_{11.08}$B$_x$ ($x = 0, 0.05, 0.2, 0.5, 0.7 \text{ wt%}$) are shown in figure 3. Just an FCC phase can be indexed on the XRD pattern of both as-cast, and deformed and heat-treated (D&H) boron-free alloys. Regarding boron-doped samples, 0.05 and 0.2 wt% boron-doped alloys also show a single FCC structure which is in the agreement with the proposed model. Further boron addition induces a second (metal boride) structure; in this case, for 0.5 and 0.7 wt% boron-doped alloys, Fe$_2$B with tetragonal structure and I$_4$/mcm space group has been detected as the M$_2$B intermetallic compound predicted by both theoretical and computational modeling methods.

Rietveld Analyses has been carried out to specify the amount of iron boride phase in 0.5 and 0.7 wt% boron-doped alloys. Rietveld analysis (table 6) reveals that in 0.5 and 0.7 wt% boron doped alloys in addition to FCC phase, 4.6 and 6.1% volume fraction Fe$_2$B phase take place respectively, where these amounts decrease to 2.7 and 5.4% in D&H samples.

This is thought to stem from higher temperatures and period provided particularly by heat-treatment and annealing process, to boron atoms to segregate at high angle grain boundaries to reduce the mixing Gibbs free energy.

The SEM images for microstructural analysis are presented in figures 4 and 5.

**Table 6. Results of Rietveld analysis for 0.5 and 0.7 wt% Boron doped alloys.**

| MEA         | Condition | FCC Content (%) | Fe$_2$B Content (%) | GOF     |
|-------------|-----------|-----------------|---------------------|---------|
| 0.5 wt% B-doped | AC        | 95.4            | 4.6                 | 1.6493  |
| 0.7 wt% B-doped | AC        | 93.9            | 6.1                 | 1.3212  |
| 0.5 wt% B-doped | D&H      | 97.3            | 2.7                 | 1.02    |
| 0.7 wt% B-doped | D&H      | 94.6            | 5.4                 | 1.03    |
FCC phase is also the primary phase of the alloy, the boron addition modifies solidification behavior of the system, where FCC and Fe2B-type boride are formed simultaneously during solidification. The final structure of thermomechanical treated samples is composed of a dendritic region with Fe2B precipitates where the interdendritic region of as-cast samples have been spheroidized and precipitated at the grain boundaries and within the FCC matrix through the thermomechanical process.

Figure 6 and table 7 provide the results from tensile tests and microhardness measurements. The performed mechanical tests show an increasing manner in both strength and hardness values by increasing the boron amount.

5. Discussion

Coupling the CALPHAD simulation to the microstructural characterization, the following solidification sequence was proposed to both boron-free and boron-containing alloys: the sample starts to solidify with the formation of BCC grains, segregating Fe, Mn, Al, Ni and B into the liquid. At the final stages, FCC takes place as a final structure where with further boron addition (higher than 0.05 in this case) FCC dendrites and Fe2B-type borides solidifies. In spite of both XRD and SEM results which show a single phase structure when x = 0.05 and 0.2, there is still a chance of the formation of Intermetallics at the grain boundaries even for 0.05 wt% boron-doped alloy, which is not detectable by these methods and needs for further investigations. The morphology of
Figure 5. SEM images of D&H samples of (a) 250x, and (b) 2500x. The composition code for each sample is located in the upper left corner of the related image.

Figure 6. Stress-Strain curves of D&H samples.
the alloys generally depends on its freezing range, the temperature gradient in the liquid, the heat extraction and the surface energy [31, 32]. Where the other parameters for the all fabricated alloys are the same, the surface energy is thought to be the key parameter in the transition of equiaxed grains to the dendritic structure. It is thought that by further boron addition (≥0.2 wt%), boron atoms increase the surface energy and induce an energy barrier which causes anisotropic grain growth in the favored directions leading to dendritic structures. On the other hand, SEM images (figure 7) emphasizes on the influence of boron addition on the microstructure.

**Table 7. The results of Hardness measurement.**

| MEAs       | HV  | SD  | HRC | SD  | HV  | SD  | HRC | SD  |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Boron-free | 219 | 10  | 15  | 2   | 212 | 10  | 14  | 2   |
| 0.05 wt% B-doped | 267 | 16  | 25  | 3   | 234 | 14  | 19  | 3   |
| 0.2 wt% B-doped | 408 | 78  | 41  | 7   | 249 | 25  | 21  | 5   |
| 0.5 wt% B-doped | 475 | 50  | 47  | 4   | 338 | 17  | 34  | 2   |
| 0.7 wt% B-doped | 538 | 89  | 51  | 6   | 332 | 15  | 32  | 2   |

*SD: Standard Deviation

**Figure 7.** SEM images of (a) A-C, and (b) D&H samples of 600x magnification, which is used to graine size measurements. The composition code for each sample is located in the upper left corner of the related image.
| Phase content | 0.05 wt% B-doped | 0.2 wt% B-doped | 0.5 wt% B-doped | 0.7 wt% B-doped | 1.0 wt% B-doped |
|---------------|------------------|------------------|------------------|------------------|------------------|
| MEA Condition  | AC + Fe2B       | AC + Fe2B       | AC + Fe2B       | AC + Fe2B       | AC + Fe2B       |
| Microstructure| FCC + Fe2B      | FCC + Fe2B      | FCC + Fe2B      | FCC + Fe2B      | FCC + Fe2B      |
| Average Grain Size (μm) | 39 ± 7, 52 ± 6 | 40 ± 7, 53 ± 6 | 40 ± 7, 53 ± 6 | 43 ± 7, 56 ± 6 | 45 ± 7, 58 ± 6 |
| HRC           | 71.4 ± 7        | 151 ± 7         | 155 ± 6         | 164 ± 6         | 170 ± 6         |
| YS (MPa)      | 50 ± 6, 54 ± 6, 58 ± 6 | 49 ± 10, 53 ± 11 | 49 ± 10, 53 ± 11 | 44 ± 10, 53 ± 11 | 44 ± 10, 53 ± 11 |
| UTS (MPa)     | 70.4 ± 6, 74 ± 4 | 81.2 ± 6, 84 ± 6 | 81.2 ± 6, 84 ± 6 | 87 ± 6, 90 ± 6  | 92 ± 6, 95 ± 6  |
| TE (%)        | 7.4 ± 2         | 7.2 ± 2         | 7.4 ± 2         | 7.2 ± 2         | 7.4 ± 2         |
| ED (g/cm³)    | 6.48 ± 0.16     | 6.48 ± 0.16     | 6.48 ± 0.16     | 6.48 ± 0.16     | 6.48 ± 0.16     |

Table 8: The summary of chemical, microstructural and mechanical characterization of boron-free and boron-doped MEAs.

1. ed*: experimental density

* ed: experimental density
as the grain size refiner agent. In both cases (ac and D&H samples) increasing of boron content has obviously led to finer grains. Zhang et al [33] believe that ‘this result is due to the rapid diffusion of boron elements into the matrix microstructure and the aggregation at the grain boundaries to prevent the grain growth’. Furthermore, grain refinement is also involved in inhibiting effect of the grain growth of boron in a solid solution.

Table 8 summarizes the results of chemical, microstructural and mechanical characterization of boron free and boron doped Fe_{52.71-x}Mn_{31.11}Al_{5.09}Ni_{11.08}B_x MEAs. The table also illustrate the grain size refinement effect of boron addition by its numerical values.

The table 8 shows that boron addition has a positive effect on grain size reduction where just by 0.05 wt% boron addition the grain size has been almost halved (from 71.8 μm to 39.7 μm) compare to boron free as-cast sample. Moreover, it is observed that as the boron level increases, the hardness value increases, the same mechanism which is used in low alloy steels to increase the hardness level.

The 0.7 wt% b-doped alloy shows the highest yield and ultimate tensile properties. The thermomechanical process resulted in increasing the yield strength by ∼50% (from 151 MPa to 222.5 MPa) and ultimate tensile strength by ∼15% (from 476 MPa to 543 MPa) - in 0.7 wt% boron doped alloy- at comparable ductility. The improvement of room-temperature tensile properties demonstrates the success of the proposed GB alloying strategy and positive effect of spheroidized iron boride intermetallics for MEAs. Just by 0.05 wt% boron addition both yield and ultimate tensile properties of the alloy has been improved due to effective grain size reduction at even better ductility. However, the transition of the equiaxed grains to the dendritic microstructure in 0.2 wt% b-doped alloy has decreased the tensile property and ductility of the alloy, regardless of the finer grains compare to 0.05 wt% b-doped alloy. Smaller dendrites led to higher ductility of the product as expected (in the case of 0.5 wt% b-doped alloy compare to 0.2 wt% b-doped alloy). On the other hand, the finer dendrites in the presence of spheroidized iron borides have enhanced the mechanical properties of the alloy. Although further amounts of Fe,B intermetallic phase (5.4% in 0.7 wt% b-doped alloy compared to 2.7% in 0.5 wt% b-doped alloy) has improved mechanical properties of the alloy, it has caused a decrease in ductility due to the higher amount of brittle iron boride phases. On the other hand, the experimental densities suggest ∼8%–9% reduction in density compared to DP 600 steel (where their density is approximately 7.874 g cm⁻³) and ∼6%–8% decrease in density compared to HSLA steels (where their density is approximately 7.80 g cm⁻³).

To sum up, the results show that decoration of grain boundaries via boron addition is an efficient individual method to optimize the strengths of metallic materials through (I) grain size reduction and (II) interface hardening (enhanced grain boundary cohesion) where the ductility remains roughly the same. Overall, boron leads to the formation of a composite with hard borides where it changes the matrix/precipitate configuration to a more ductile one. This can completely explain the reason of why the strengths of boron-doped alloys are higher than the boron-free alloy while having approximately the same ductility. Moreover, regarding the obtained results, it can be said that this method is also applicable to other single (FCC) phase MEAs as well as HEAs, since it improves the GB properties, but does not affect the bulk deformation mechanisms.

6. Conclusions

Based on phase diagrams and thermodynamic calculation, Fe_{(52.71-x)}Mn_{31.11}Al_{5.09}Ni_{11.08}B_x (x = 0, 0.05, 0.2, 0.5, 0.7 wt%) MEAs were successfully designed. The conclusions are listed as follows:

1. The model proposes that benefiting from high entropy principles, by the enthalpy of mixing values in the range of −15 and 5 kJ mol⁻¹ and Ω parameters higher than 1.1, obtaining a single-phase structure up to 6.6% atomic size difference (δ parameter), is still possible.

2. Even addition of minor alloying elements (boron in this case) with a careful arrangement of enthalpy of mixing (ΔH_{mix}), Ω parameter, and (b) parameter could lead to single solid solution phases.

3. XRD results demonstrate that up to 0.2 wt% boron addition results in a single FCC phase, while further boron addition (i.e. 0.5 and 0.7 wt%) promotes the formation of metal borides which is in the agreement with the proposed model.

4. Boron addition has a positive effect on grain size reduction of the system where just by 0.05 wt % boron addition the grain size has been almost halved compared to boron free as-cast sample.

5. Finally, the results show boron addition in general is an efficient site-specific manipulation method that allows optimization of the strengths through grain size reduction and enhanced grain boundary cohesion without sacrificing ductility.
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