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Insights into the phase diagram of the CrMnFeCoNi high entropy alloy using electromagnetic melting and casting

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Abstract

High entropy alloys are single phase metallic materials, composed of more than 4 elements in equi-atomic proportion which is the maximum in the configurational entropy. In order to study the thermodynamics of those alloys, an equimolar CrMnFeCoNi HEA was processed by electromagnetic melting, casting and annealing under varying conditions (cooling rate and annealing duration) and the evolution of the structure and microstructure was studied. After casting, a dendritic microstructure was formed whose characteristic length depends on the cooling rate. Annealing leads to a chemical homogenization of the microstructure. Indeed a true solid-solution down to the atomic scale was evidenced in an HEA by atom probe tomography. It was shown that this face-centered cubic single-phase solid solution is the high temperature stable state of the equimolar CrMnFeCoNi alloy. By analogy with completely miscible binary alloy, the CrMnFeCoNi HEA can be described by a schematic phase diagram of the CrFeCo - MnNi system consisting of a liquidus and a solidus.

Key words : high entropy alloy, atom probe tomography, phase diagram

Introduction

In industrial fields like aeronautics, aerospace or energy production, steels and nickel-based super-alloys are commonly used. Those conventional metallic alloys are composed of one principal element, or rarely two, and an addition of several minor elements, which generally have a concentration lower than few atomic percents and whose role is to tailor the properties. For a long time, development of alloys was restricted to this model – one principal element and minor elements, so as to avoid complex microstructures and especially the precipitation of intermetallic compounds, which commonly lead to a fragile mechanical behavior. In 2004, Cantor *et al.* [1] produced a multi-component alloy composed of Cr, Mn, Fe, Co and Ni in equimolar proportions, and this alloy was mono-phase. Then Yeh *et al.* [2] pointed out the critical role of the configurational entropy to form a multi-element solid solution and proposed the name of “high entropy alloys” (HEA). HEA were defined as alloys composed of five or more principal elements in equimolar ratios or more generally with concentrations between 5 and 35 at. %. Very promising mechanical properties are expected from such a multi-component solid solution. Indeed, as exposed by Zang *et al.* [3], the presence of atoms with different sizes should result in a great distortion of the lattice and thus in mechanical strengthening. Compared to conventional solid solution, where the alloying element concentration is only of few atomic percents, strengthening in HEA should be significantly enhanced. The aim of this work is to investigate the evolution of the structure and microstructure of the equimolar CrMnFeCoNi high entropy alloy during processing under varying conditions (cooling rate and annealing duration). Electron Probe MicroAnalysis (EPMA) and Atom Probe Tomography (APT) were used for the characterization of as-cast and as-annealed alloys.

Experimental

Raw Co, Cr, Fe, Mn and Ni metals with a purity exceeding 99.9 wt % were used and preparation of the alloys was performed using high frequency electromagnetic induction melting. Suction or twin roll casting were then performed to shape the CrMnFeCoNi ingots providing respectively with rod with a diameter of 3 mm and a length of around 10 cm at the cooling rate of $10^3 \text{ K}\cdot\text{s}^{-1}$ and plate with a thickness about 500 μm and a length about 1 m at the cooling rate of $10^4 - 10^5 \text{ K}\cdot\text{s}^{-1}$. The sample obtained by suction casting was annealed at 1100°C for 1 h and 6 h under He atmosphere. The heating rate was of 10°C/min and at the end of annealing, still maintained in the He atmosphere, the sample was quickly cooled down. Electron probe micro-analysis (EPMA) was done with a Cameca SX100 device. X-ray maps and atomic quantitative measurements were generated. To prepare Atom Probe Tomography (APT) samples, rods of 0.25 x 0.25 x 10 mm³ were cut from the bar obtained by suction casting and were subsequently polished to a tip diameter of around 50 nm by electropolishing at room temperature at 20 V in a solution of monobutoethanol with 2 % of perchloric acid.

Then an energy compensated wide angle Cameca atom probe was used at 80 K, with electric pulses with a repetition rate of 30 kHz and a pulse fraction of 20 %. For the as-cast HEA (HEA-I+SC), three analyses were undertaken, which represents altogether 2.0 million detected atoms or equivalently a total volume of 52.10^3 nm^3 . For the annealed HEA (HEA-I+SC+A2), 2 analyses were undertaken, which represents 1.3 million detected atoms or equivalently a volume of 30.10^3 nm^3 .

Results and discussion

Alloy structure was reported as is fcc elsewhere [4]. EPMA gives evidence that after induction, the HEA alloy exhibits some composition fluctuations at a micrometer scale as can be seen on the Fe X-ray map obtained by EPMA (Figure 1a). Those fluctuations are isotropic and have a length scale of 15 to 20 μm . The length scale is defined as the distance between the centre of two neighbor Fe-enriched areas. After suction casting, such fluctuations are still present, with a finer length scale about 5 μm and a dendritic-like morphology (Figure 1b). The dendrites are enriched in Cr, Fe and Co whereas the interdendritic areas are enriched in Mn and Ni. Finally, after an annealing at 1100°C for either 1 h or 6 h, the HEA alloy appears homogeneous on the X-ray map (Figure 1c and d). According to the EPMA quantitative composition measurement, all samples have the expected equimolar average composition but with varying standard deviations, which reflect the observed composition fluctuations. Annealing during 6 h has homogenized the alloy within the limit of detection of EPMA. It has to be noted that, according to Vegard's law, dendrites and interdendrites have a maximum difference of lattice parameter of 0.001 nm, which is of the order of the XRD uncertainty and thus could not be detected.

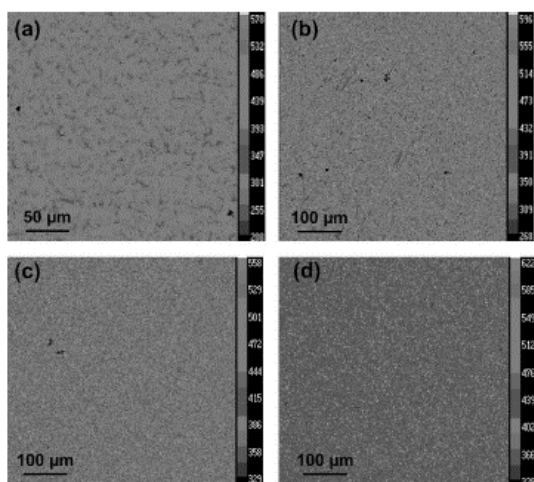


Fig. 1: X-ray Fe maps obtained by EPMA of the HEA alloy after (a) induction (HEA-I), (b) suction casting (HEA-I+SC), (c) annealing at 1100°C during (c) 1 h (HEA-I+SC+A1) and (d) 6 h (HEA-I+SC+A2). The grey scale indicates the intensity of the Fe

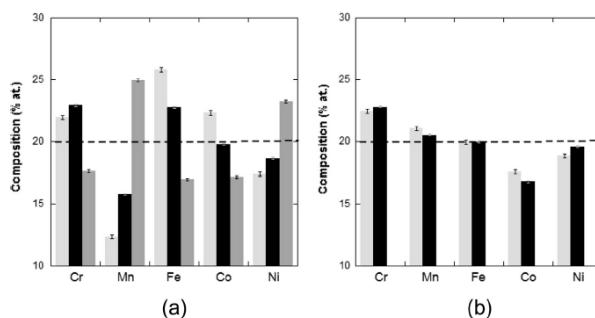


Fig2 : Chemical compositions as measured by APT in (a) the as-cast HEA (HEA-I+SC) and in (b) the annealed HEA (HEA-I+SC+A2)(b). Columns with different colors (light grey, black and dark grey) correspond to different analyzed areas. Error bars correspond to the standard deviation 2σ . The horizontal dashed line represents the nominal composition.

HEA alloy was also produced by twin rolling instead of suction casting, during which the cooling rate is around 10 to 100 times faster than during suction casting. The edge of the plate is homogeneous whereas some dendrites are present in the core. It is very likely due to a gradient of cooling rate between the core and the side. Composition measurements (not shown here) of the core are similar to the ones of HEA after annealing while composition measurements of the core have slightly smaller standard deviations than the HEA after suction casting. Thus high temperature annealing and sufficiently fast cooling can both form a homogeneous phase in CrMnFeCoNi alloy at the micrometer scale.

To study the elements distribution at a nanometer scale, atom probe tomography (APT) analyses were performed. The average chemical composition measurements are plotted on Figure 2. For the as-cast alloy (Figure 2(a)), it can be seen that the measured composition is different from the nominal composition and that it varies from one analysis to another. More precisely, the composition variations of Ni and Mn on the one hand and of Cr, Co and Fe on the other hand are correlated. This is in agreement with EPMA measurements. It can be deduced that analyses 1 and 2 (light grey and black), which exhibit lower Ni and Mn contents than the nominal composition, were carried out on within a dendrite

whereas the analysis 3 (dark grey), which exhibits a higher Ni and Mn contents than the nominal composition, was carried on within an interdendrite area. The data points corresponding to dendrites are more depleted in Ni and Mn than the one measured by EPMA. This can be explained by the fact that smaller volumes (typically $10^{-5} \mu\text{m}^3$) are analyzed by APT than by EPMA (typically $1 \mu\text{m}^3$). Consequently a measurement by EPMA averages a larger range of the composition fluctuations of the dendritic microstructure. For the annealed HEA (Figure 2(b)), the measured compositions of each analysis are very close and there is no correlation anymore between composition variations of Ni and Mn on the one hand and of Cr, Co and Fe on the other hand. Thus it can be concluded that annealing at 1100°C during 6 h has homogenized the alloy down to the nanometric scale. More precisely, it can be noted that in both analyses of the annealed HEA, there is a slight depletion of Co and Ni and a slight enrichment in Cr compared to the nominal composition. The same tendency, in a smaller extent, was also observed by EPMA measurements. Thus this difference of composition compared to the nominal one is very likely to be due to a macro-segregation, and not to a lack of homogenization of the previous dendritic structure. A low and heterogeneous concentration of N and C (not plotted) was also detected by APT. Indeed there are between 0.02 and 0.17 at. % of N and between 0 and 0.033 at. % of C in the as-cast HEA and there are between 0.09 and 0.28 at. % of N and between 0.03 and 0.04 at. % of C in the annealed HEA. The APT analysis of the as-cast and annealed HEA are depicted in 3D on Figure 3 (a) and Figure 4 (a). The atom distribution appear to be randomly distributed. To quantitatively confirm this, first, concentration profiles were plotted and compared to the average concentration and to its standard deviation. The standard deviation is calculated as the variance square root of a random distribution of atoms whose concentration is the average of the studied sample. Mn and Fe concentration variations are most of the time smaller than the standard deviation for both as-cast and annealed samples (Figure 3 (b) and Figure 4 (b)).

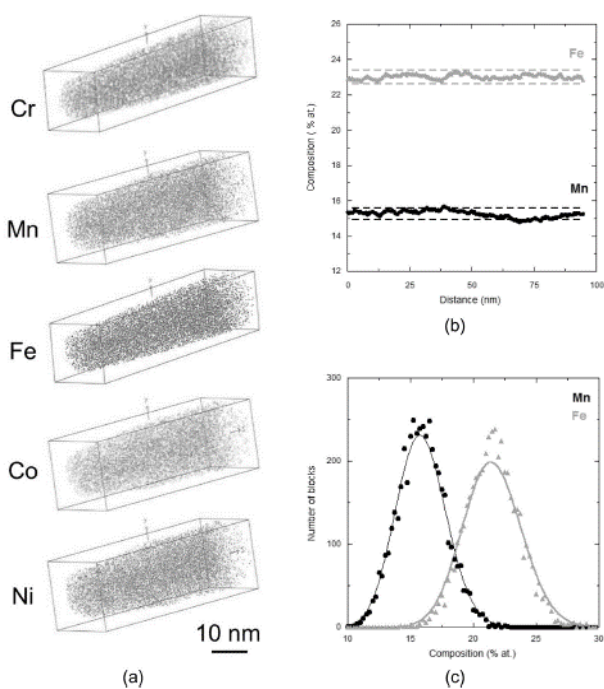


Fig. 3 : APT characterization of the as-cast HEA (HEA-I+SC). (a) 3D reconstructions, (b) concentration profiles of Mn and Fe compared to the average measured concentration (bold line) and to the standard deviation (dashed line) and (c) frequency distributions of Mn (full black circles) and of Fe (full grey triangles) compared to a binomial distribution (black and grey lines)

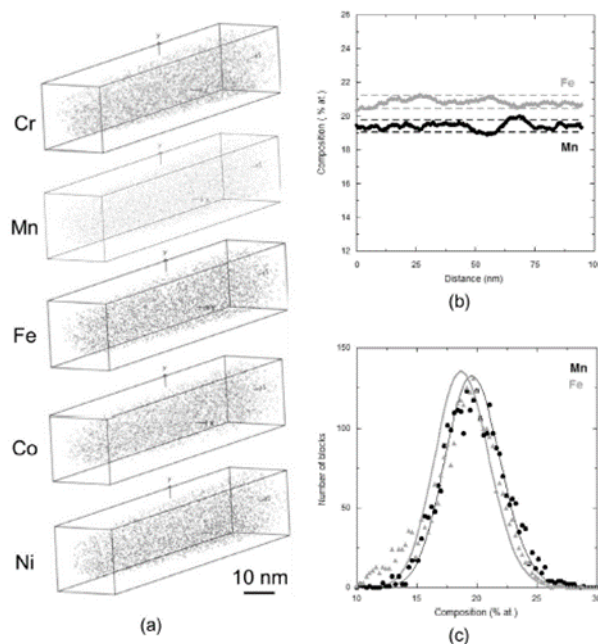


Fig. 4: APT characterization of the annealed HEA (HEA-I+SC+A2). (a) 3D reconstructions, (b) concentration profiles of Mn and Fe compared to the average measured concentration (bold line) and to the standard deviation (dashed line) and (c) frequency distributions of Mn (full black circles) and of Fe (full grey triangles) compared to a binomial distribution (black and grey lines).

There are few points where Mn or Fe concentrations are slightly larger than the standard deviation but since there are

never correlated, it can be neglected. Second Mn and Fe frequency distributions were plotted for both the as-cast and annealed HEA and they are similar to a binomial distribution (Figure 3 (c) and Figure 4 (c)). Similar concentration profiles and frequency distributions were obtained for Cr, Co and Ni (not shown here). Thus both the as-cast and annealed HEA have neither nanoprecipitates nor nanoscale chemical fluctuations.

Thermal analysis of the homogeneous HEA after annealing 1100°C for 6 h (HEA-I+SC+A2) was performed by DSC between room temperature and 1400°C. A single endothermic peak is attributed to the melting of the alloy. The onset, maximum and area of this peak correspond to the solidus (1290°C), liquidus (1340°C) and melting enthalpy (13 kJ.mol⁻¹) respectively. Since the solidus and liquidus are close to each other, the liquidus value has to be considered as an upper limit [5].

The solidification of high entropy alloys can be compared to the solidification of binary alloys which have a complete miscibility. By analogy, a schematic phase diagram of a pseudo-binary system (CrFeCo)-(MnNi) can be proposed, with the solidus and liquidus temperatures of respectively 1290 and 1340°C. Then microstructure and chemical distribution can be assumed during solidification using model such as Gulliver-Scheil [6].

Conclusion

An equimolar CrMnFeCoNi alloy was produced by melting, solidification with various cooling rate and annealing for various durations. The obtained alloy was characterized after each step using electron probe micro-analysis and atom probe tomography. The main results are :

- True solid-solution down to the atomic scale was evidenced.
- By analogy with completely miscible binary alloy, the CrMnFeCoNi HEA can be described by a pseudo-binary phase diagram of the CrFeCo-MnNi system consisting of a liquidus and a solidus. When the cooling is slow enough, dendrites enriched in Cr, Fe and Co and interdendrites enriched in Mn and Ni are formed.
- To homogenize the dendritic structure, the duration and temperature of annealing can be optimized by measuring the characteristic length of the dendritic structure and then by using the diffusion coefficients measured by Tsai *et al.* [7] and the microsegregation model of Kattamis *et al.* [8].

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