From high entropy alloys to diluted multi-component alloys: Range of existence of a solid-solution

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ABSTRACT

In order to systematically compare high entropy alloys (HEA) and conventional diluted multi-component alloys and to observe the transition between both, 13 $Cr_xMn_xFe_xCo_xNi_{100-4x}$ multi-component alloys, where x takes values between 2 and 25, were processed so as to reach the stable state and then characterized. A unique fcc solid-solution is formed for a wide range composition, spanning from 0 to 90 at.% of Cr, Mn, Fe and Co. When the sum of Cr, Fe, Mn and Co contents is larger than 90 at.%, the system demixes into two quaternary phases. The existing thermodynamics models are unable to predict the range of existence of the solid-solution for the studied alloys. No microstructural transition between HEA and conventional diluted alloys is observed. The maximization of configurational entropy appears to be neither a sufficient nor a necessary condition to form a HEA. Consequently a new definition for HEA is needed.

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1. Introduction

In order to meet the always more demanding industrial requirements, new concepts of materials are developed. One of them is the so-called high entropy alloys (HEA). HEA are multi-component alloys (MCA) in which all components are very concentrated, in such a way that the conventional distinction between solvent and solute is not possible anymore, and which form a true solid-solution, or in other words a single crystalline structure on which all elements are randomly distributed. This new alloying strategy relies on the maximization of configurational entropy, which should stabilize the solid-solution and prevent the formation of multi-phased system, including fragile intermetallic compounds [1]. Indeed, by definition, configurational entropy increases with the number of elements and when the composition gets closer from the equimolar proportion. Subsequently, a quantitative definition of HEA was proposed: alloys composed of five or more elements in equimolar ratios or, in an extended definition with concentration between 5 and 35 at.% [1]. It was thought that such a concentrated multi-component solid-solution could be very distorted and consequently combine strength and ductility [2]. Thus very advantageous mechanical properties are expected from HEA.

At first, several quinary equimolar alloys, such as CrMnFeCoNi [3,4], VNbMoTaW [5] or TiZrNbHfTa [6], were found to form a true solid-

solution as expected. However multi-phase microstructures were also often discovered, like in the alloy AlCrFeCoNiCu [7,8]. It leads to the development of many models [9–12] in order to predict appropriate composition for HEA. Although those models significantly improve the understanding of HEA thermodynamics, this is still an on-going research topic. Especially, the predictive characteristic of those models still has to be proven, despite they all clearly establish that maximizing configurational entropy is not a sufficient condition to form a multi-component solid-solution. Thus there is no reason to focus on quinary equimolar alloys, as it was done in early studies. Recently, alloys such as $Cr_2Mn_{27}Fe_{40}Co_5Ni_{26}$ [13], $Cr_{10}Mn_{40}Fe_{40}Co_{10}$ [14], $Cr_4Mn_{28}Fe_{40}Ni_{28}$ [15] or $Ti_{10}Cr_{18}Fe_{18}Co_{27}Ni_{27}$ [16], were produced and some of them were found to be single-phased. However, up to now, non-equimolar compositions have never been systematically studied.

In this context, it is proposed to study multi-component alloys (MCA), including non-equimolar compositions within the Cr-Mn-Fe-Co-Ni system. This system was chosen because this is the one whose thermodynamic stability is the most known, at least for the equimolar alloy. Indeed, it was experimentally proven that, for the equimolar alloy, the face-centered cubic true solid-solution is the thermodynamical stable state at high temperatures (i.e. 1100 °C) [4] but that stable additional phases precipitate at medium temperatures (i.e. 700 °C or lower) [17–19]. The objectives of this study are (i) to determine the range of existence of the solid-solution as a function of the composition as well as (ii) to compare conventional diluted solid-solutions with high entropy alloys and to observe the transition between both. Since Ni is the only element of the system to be face-centered cubic at room temperature, like the equimolar CrMnFeCoNi HEA, it was chosen as the solvent while Cr, Mn, Fe and Co are considered as solute and are in equal

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proportion. Of course, the distinction between solute and solvent becomes irrelevant when the composition comes close to the equimolar proportion. 13 $Cr_xMn_xFe_xCo_xNi_{100-4x}$ alloys, with x varying between 2 and 25, were processed and characterized by X-ray diffraction and energy dispersive spectroscopy coupled with scanning electron microscopy.

2. Materials and methods

13 $Cr_xMn_xFe_xCo_xNi_{100-4x}$ multi-component alloys (MCA) were studied, where x takes the values of 2, 3, 4, 7.5, 10, 12.5, 15, 17.5, 18.75, 20, 22.5, 23.75 and 25. It is underlined that those 13 alloys do not permit to explore the entire range of chemical composition of the quinary Cr-Mn-Fe-Co-Ni system. Samples are named according to their Cr, Mn, Fe and Co content which is equal to 4x. As an example, $Cr_2Fe_2Mn_2Co_2Ni_{92}$ and $Cr_{20}Fe_{20}Mn_{20}Co_{20}Ni_{20}$ alloys are respectively named MCA-8 and MCA-80. For low values of x, 4x represents the solute content. All alloys were prepared with the same procedure, which has been previously developed for the equimolar alloy CrMnFeCoNi [4]. Raw Co, Cr, Fe, Mn and Ni metals with a purity exceeding 99.9 wt.% were used. To remove eventual traces of oxides, appropriated chemical etching and mechanical polishing were performed on raw metals before the melting process. First, alloys were prepared by high frequency electromagnetic induction melting in a water-cooled copper crucible under He atmosphere. Then suction casting was performed to shape the CrMnFeCoNi ingots. The cooling rate was estimated at about 10^3 K·s^{-1} and a rod with a diameter of 3 mm and a length of around 10 cm was obtained. The rods were cut into slices of around 2–3 mm of length. Finally the samples, which were wrapped in a tantalum sheet, were annealed at 1100 °C for 6 h under an He atmosphere. The heating rate was of 10 °C·min^{-1} and at the end of annealing, still maintained in the He atmosphere, the samples were quickly cooled down. Because of this last processing step, it is reasonably assumed that the studied alloys represent the high temperature (i.e. 1100 °C) stable state.

X-ray diffraction (XRD) was performed in a PANalytical X'Pert Pro diffractometer using the Co–Kα radiation at a wavelength of 0.178897 nm. A Merlin Zeiss microscope, which is equipped with a field emission gun, was used for Scanning Electron Microscopy (SEM). The chemical composition was measured thanks to energy dispersive spectroscopy (EDS). Maps of the five elements were recorded at a magnification of ×1000. Between 10 and 20 randomly distributed point measurements were also recorded. The given compositions and the corresponding uncertainties are respectively the average and the standard deviations of those measurements. For the two-phased samples (i.e. MCA-95 and MCA-100), point measurements were split into the two phases.

3. Results

XRD patterns as well as Cr and Co SEM-EDS mappings of MCA-90, MCA-95 and MCA-100 are depicted on Fig. 1. For MCA-90 and MCA-95, Fe, Mn and Ni EDS mappings (results not shown here) are similar to Co mappings. Fig. 2 presents BSE image and Cr, Fe, Mn and Co EDS mappings of MCA-100. First, the XRD pattern of MCA-90 exhibits only four peaks corresponding to a face centered cubic phase. On the SEM-EDS mappings, MCA-90 appears homogeneous down to the micrometer scale and according to the EDS quantitative composition measurements the sample has the expected composition. Some nano-precipitates have already been observed by atom probe tomography or transmission electron microscopy in HEA alloys which were as-cast or which have been briefly annealed [7,20,21]. Such nano-precipitates cannot be detected either by XRD or by SEM-EDS. However nano-precipitates are metastable and, if they would have existed in the as-cast MCA-90 sample, they would very likely have grown up to the micrometer scale during the long and high temperature annealing. Thus it is considered that the observed homogeneity of MCA-90 at the micrometer scale implies an

homogeneity down to nanometer scale and that MCA-90 is composed of a true and unique multi-component solid solution. The 11 MCA-4x alloys with 4x ≤ 90 at.% exhibit similar XRD and SEM-EDS results than MCA-90. In other words, they are also solely composed of a solid-solution.

However, MCA-95 and MCA-100 are not single-phased. The XRD pattern of MCA-95 still exhibits the four peaks which are characteristic of the fcc phase observed in MCA-90 but it also exhibits additional peaks which indicate the presence of a second phase. This is confirmed by SEM-EDS mappings where elongated and Cr-enriched precipitates are observed. Those precipitates have a length ranging from 2 to 18 μm and a width ranging from 2 to 4 μm. The volume fraction was determined by image analysis of the Cr EDS-SEM mapping (Fig. 1) and is around 4%. As shown on the measurements gathered in Table 1, the precipitates are enriched in Cr (36.6 ± 0.2 at.%) compared to the main phase (23.7 ± 0.1 at.% of Cr). No depletion of Cr is measured in the main phase (the Cr nominal content is of 23.75 at.%). This is due to the very low volume fraction of the Cr enriched precipitates. Indeed, based on the volume fraction and Cr content of the precipitates as well as on the Cr nominal content, a Cr depletion in the main phase of 0.5 at.% is calculated. This is too close from the uncertainty of EDS measurements to be detected. The XRD peaks of the fcc phase can be attributed to the main phase since the composition is very similar to the one of MCA-90. The XRD pattern of MCA-100, which is actually a quaternary equimolar alloy, exhibits numerous peaks reflecting a complex microstructure. This is in agreement with [22]. EDS mappings reveal two phases with irregular shape and characteristic dimension in the micrometer range. The first one is Cr-enriched (33.5 ± 0.2 at.% of Cr), is partially percolated and has a volume fraction, which was also determined by image analysis, of around 30%. The second one is Cr-depleted (21.9 ± 0.1 at.% of Cr) and is surrounding the Cr-enriched phase. The exact composition of both phases is given in Table 1. The microstructure of MCA-100 resembles the one due to a spinodal decomposition, which exists in the Fe-Cr system [23,24]. A deeper study is needed to confirm it.

To summarize, in the Cr-Mn-Fe-Co-Ni system, the fcc multi-component solid solution is the high temperature stable state for a large range of composition: between 8 and 90 at.% of Cr, Fe, Mn and Co or equivalently between 10 and 92 at.% of Ni. When the sum of Cr, Fe, Mn and Co contents is larger than 90 at.%, the system demixes into two phases, which contains all elements and are either enriched or depleted in Cr.

4. Discussion

Following the Boltzmann's hypothesis, the configurational entropy change per mole during the formation of a solid-solution of n component can be defined as [2]:

$$\Delta S_{conf} = -R \sum_{i=1}^{n} c_i \cdot \ln c_i$$

where R is the gas constant and c_i is the concentration of element i. By applying this formula to the $Cr_xMn_xFe_xCo_xNi_{100-4x}$ studied alloys, the configurational entropy is now expressed as:

$$\Delta S_{conf} = -R \cdot [4x \cdot \ln(x) + (100-4x) \cdot \ln(100-4x)]. \tag{1}$$

Using this formula, the configurational entropy of $Cr_xMn_xFe_xCo_xNi_{100-4x}$ MCA is plotted according to the sum of Cr, Fe, Mn and Co contents and is compared to the range of existence of the solid-solution (Fig. 3). It can be seen that there is no correlation between the configurational entropy and the formation of a solid-solution. More precisely, maximizing configurational is neither a sufficient nor a necessary condition to form a solid-solution. Indeed, for example, alloys MCA-95 and MCA-8 have configurational entropy of respectively 12.6 and