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On the influence of Mn on the phase stability of the $CrMn_xFeCoNi$ high entropy alloys

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ABSTRACT

The *fcc* phase of the equiatomic high entropy alloy, CrMnFeCoNi, has been recently shown to be unstable at temperatures below 800 °C. However, the stability of the constituent CrFeCoNi quaternary alloy, which forms the basis of many other high entropy systems, remains under debate and the existing literature contains very little long duration heat treatment data. Here, the phase equilibria of CrFeCoNi and $CrMn_{0.5}FeCoNi$ are assessed following 1000 h exposures at 500, 700 and 900 °C. Prior to thermal exposure the cast alloys were homogenised and shown to exist as single phase *fcc* solid solutions. In line with previous reports, Cr rich particles were observed on the grain boundaries following the prolonged exposures but detailed electron microscopy showed that these features were $M_{23}C_6$ carbides resulting from the unintentional incorporation of C during production. However, no evidence was found for any other phase formation during the heat treatments of either alloy, in direct contrast to the results for CrMnFeCoNi. Consequently, it is concluded that, within the limits of the temperature and times considered, the solid solution phases of both CrFeCoNi and $CrMn_{0.5}FeCoNi$ are stable and that Mn has a destabilising influence when present in sufficient concentrations. This change in behaviour occurs for a Mn content between 11.1 and 20 at.%.

1. Introduction

Within the last two years, experimental results have shown that the equiatomic high entropy alloy, CrMnFeCoNi, originally thought to be a stable single phase solid solution, is susceptible to the formation of the topologically close packed sigma phase at temperatures between 500 and 800 °C [1–3]. It has also been identified that this alloy undergoes more complex phase decompositions at lower temperatures resulting in multiple phases [2,4].

In contrast, the CrFeCoNi quaternary alloy, which is the basis of many other high entropy alloy systems, is still widely regarded to be stable as a single solid solution phase at all temperatures below the solidus. Several studies have reported that CrFeCoNi exists as a single *fcc* solid solution phase based on data from cast material, gathered using laboratory diffraction techniques and relatively low-resolution electron microscopy [5–8]. Other investigations have utilised various annealing heat treatments prior to characterisation, yet the single solid solution phase remains the only observed microstructural constituent [5,9,10]. One study also used neutron diffraction and anomalous X-ray scattering to study the structure of the material following heat treatment at 480 °C for 336 h. Again, the data indicated that only a single *fcc* structure was present and that no ordered phases, such as Ni_3Fe, had formed [10].

However, more recently, the apparent stability of this alloy has also been questioned by the results of publications that have studied the material with higher resolution techniques. For example, a suction-cast sample of CrFeCoNi, thought to be homogeneous from scanning electron microscopy data, was found to contain compositional fluctuations above the measurement error, when characterised using atom probe tomography [11]. Similarly, analysis of the peak profiles obtained from high-energy synchrotron diffraction revealed that the as-cast material contained at least two different *fcc* phases, with very similar lattice parameters [12].

It should be noted that materials studied in an as-cast state are highly likely to contain solidification-induced microsegregation and, therefore, the presence of these inhomogeneities will be reflected in the data gathered from any given technique that is capable of characterising the material at a corresponding length scale. The existence of elemental segregation may also influence the behaviour of the material during subsequent investigations, for example during low or

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intermediate temperature heat treatments. Avoidance of this issue is of critical importance to phase equilibria research, as highlighted by two recent reviews [13,14], both of which emphasise the need for studies of multi-component alloys to start with material that is as homogeneous as possible. Nevertheless, recent transmission electron microscopy results from CrFeCoNi have led to the suggestion that phase decomposition may be occurring in these materials during prolonged high temperature heat treatments [15].

Rather surprisingly, there is relatively little data in the literature that relates to the influence of long-term heat treatments at intermediate temperatures on the constituent phases of CrFeCoNi. One study that has characterised as-cast material subsequently exposed for 800 h at 750 °C in air reported data consistent with a single solid solution phase from scanning electron microscopy and X-ray diffraction data [16]. However, characterisation of the material in a transmission electron microscope revealed lenticular features within an *fcc* matrix. High resolution imaging of these features did not identify any clear interfaces and showed only small distortions of the lattice, on the order of 3 p.m. From these results, the authors concluded that CrFeCoNi was metastable at 750 °C and they had observed elemental clustering during the initial stages of phase decomposition, although no chemical data relating to the features were reported. In addition, when 2.4 at.% Al was incorporated into the alloy, a Cr rich phase was observed on the grain boundaries following exposure at 750 °C, which based on its measured composition, was suggested to be the sigma phase [16].

Recently, a dedicated HEA thermodynamic database has been developed (ThermoCalc TCHEA) and has been used to look at the effect of each constituent component on the phase equilibria in the CrMnFeCoNi system [17]. The thermodynamic predictions produced in this study suggested that Co and Ni support the formation of a single *fcc* phase, Fe has little effect, whilst Mn and particularly Cr destabilise the single phase state. Experimental results from eight different alloys, heat treated for times between 48 and 144 h at either 1000 or 1100 °C, were used to validate the fidelity of the predictions. Comparison of the experimental findings to the theoretical predictions revealed that the extent of the *fcc* solid solution was well described but that the database underpredicted the stability of the sigma phase. Thorough assessments of the accuracy of thermodynamic predictions, such as those presented in Ref. [17], are critical if these databases are to form the basis for alloy design activities.

Another interesting feature arising from these thermodynamic calculations were the changes in the phase equilibria for the quaternary CrFeCoNi alloy as a function of temperature [17]. As would be expected, at high temperatures ($T > \approx 650$ °C) a single *fcc* solid solution was predicted but at lower temperatures, multiple phases were predicted, including two *bcc* phases and a second *fcc* phase. Further to this, the incorporation of a small amount of Mn was predicted to introduce the sigma phase as well. However, these particular alloys were not fabricated or characterised in Ref. [17], nor were any experimental data obtained at temperatures below 1000 °C, and so these predictions have not been verified.

It is evident from this short review of the literature that there are many discrepancies in the published data with respect to the stability of the CrFeCoNi alloy. Clearly, this is a key issue to resolve in understanding the stability of the single *fcc* phase, not only from a fundamental standpoint but also given that this quaternary alloy forms the basis of several different high entropy alloy systems. In addition, if the quaternary alloy is established to be stable as a single solid solution phase, then it would demonstrate that the Mn additions are responsible for destabilising that phase and promoting the formation of the sigma phase in the CrMnFeCoNi system, consistent with thermodynamic predictions. Therefore, in the present work, we investigate the influence of Mn on the phase stability of $CrMn_xFeCoNi$ HEAs at temperatures below 1000 °C by studying two alloys, with $x = 0$ & 0.5, and comparing the results with those obtained from the equiatomic alloy, $x = 1$, which were previously reported in Ref. [1].

2. Experimental method

To investigate the role of Mn on the phase stability of alloys in $CrMn_xFeCoNi$ HEAs, two 50 g ingots were arc melted from pure elements under an inert atmosphere. The nominal Mn content of these alloys was 0 and 11.1 at.%, corresponding to CrFeCoNi and $CrMn_{0.5}FeCoNi$ respectively. To enhance the macroscopic homogeneity of the ingots, each alloy was inverted and remelted a total of five times. In line with previous work [2], the cast alloys were homogenised for 100 h at 1200 °C inside evacuated and argon backfilled quartz ampoules. Several transverse sections, approximately 10 mm thick, were taken from the homogenised ingots, each of which was encapsulated as above and thermally exposed at either 500, 700 or 900 °C for 1000 h.

Material at each stage of the process was characterised using backscattered electron imaging in an FEI Nova NanoSEM 450 scanning electron microscope (SEM), which was also fitted with a Bruker xFlash 100 detector, enabling energy dispersive X-ray (EDX) mapping of the elemental distributions. Calorimeteric data was acquired between room temperature and 1450 °C using a Netzsch 404 differential scanning calorimeter at heating and cooling rates of 10 °C min^{-1} under flowing argon. X-ray diffraction patterns were gathered using a Bruker D8 diffractometer, with a Ni filtered Cu source, between angles of 20 and 120° 2θ. Phase identification and lattice parameters were obtained from the diffraction data using the Pawley model in the TOPAS-Academic software.

Higher resolution studies of the alloys were performed using transmission electron microscopy. 3 mm discs were removed from material in different heat treatment conditions and thinned by twin jet electro polishing, using a solution of 10% $HClO_4$ in CH_3OH at −35 °C and an applied potential of 20 V. In addition, several specific sites of interest were extracted from the bulk material through focussed ion beam milling. The electron transparent samples were investigated in an FEI Talos F200X Scanning Transmission Electron Microscope (STEM), equipped with Super EDX detectors, and an aberration corrected FEI Titan, both of which were operated at 200 keV.

3. Results

3.1. As-cast and homogenised material

Backscattered electron (BSE) images of CrFeCoNi and $CrMn_{0.5}FeCoNi$ in the as-cast state are presented in Fig. 1. Both images showed that the materials had a large grained microstructure, with contrast appearing to be driven by crystal orientation rather than compositional variation. Small, black contrast particles were also observed in the as-cast microstructure of both alloys, which were identified to be oxide impurities in line with previous studies [1,18–21]. The bulk compositions of the materials, obtained by averaging five large area (500 × 500 μm) EDX scans, are given in Table 1 and were within ± 1 at.% of the target concentrations for each element in both alloys.

X-ray diffraction patterns for the alloys are shown in Fig. 2 and in the as-cast state the data contained reflections that corresponded to one *fcc* phase, with no other peaks visible above the background. The effect of Mn on the lattice parameter of the *fcc* phase was assessed by full pattern fitting using the Pawley method in TOPAS-Academic. The model for the CrFeCoNi data produced a refined lattice parameter of 3.58 ± 0.01 Å, whilst a value of 3.59 ± 0.01 Å was obtained for $CrMn_{0.5}FeCoNi$. Whilst the BSE images and diffraction data appeared to indicate that both CrFeCoNi and $CrMn_{0.5}FeCoNi$ existed as single phase materials with a homogeneous microstructure in the as-cast state, SEM based EDX mapping showed clear elemental segregation within the grains, consistent with dendritic solidification, Fig. 1.

To remove the solidification induced micro-segregation, the alloys were homogenised at 1200 °C for 100 h. This temperature was chosen to be as close to the solidus temperature of each alloy as possible, found