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Christofidou, K.A., McAuliffe, T.P., Mignanelli, P.M. et al. (2019) On the prediction and the formation of the sigma phase in CrMnCoFeNix high entropy alloys. Journal of Alloys and Compounds, 770. pp. 285-293. ISSN: 0925-8388

https://doi.org/10.1016/j.jallcom.2018.08.032

On the prediction and the formation of the sigma phase in CrMnCoFeNi$_x$ high entropy alloys

K.A. Christofidou[1], T.P. McAuliffe[1], P.M. Mignanelli[1], H.J. Stone[1] and N.G. Jones[1*]

[1]Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, CB3 0FS, UK

[*]Corresponding author ngj22@cam.ac.uk

Abstract

The almost limitless variations in potential compositions of high entropy alloys necessitates the use of computational methods when attempting to optimise for any given application. However, the accuracy of the current thermodynamic approaches commonly being used for this purpose remains under debate, as relatively few validatory studies have been performed. Within the CrMnFeCoNi family of alloys, the formation of the σ phase and how it is influenced by compositional variations is of particular interest for elevated temperature structural applications. Here, the role of Ni on the formation of the σ phase has been studied through a systematic series of CrMnFeCoNi$_x$ alloys, $0 \leq x \leq 1.5$, following 1000 hour exposures at temperatures typically found to promote σ formation. Ni was found to have a significant effect on the phase stability of these alloys, suppressing the σ phase such that a single solid solution phase was the only stable phase in the CrMnFeCoNi$_{1.5}$ alloy, whilst the CrMnFeCo alloy formed the σ phase during solidification. The corresponding thermodynamic predictions varied dramatically from the experimentally observed microstructures, indicating that the underlying databases require further optimisation. Interestingly, it was found that a relatively simple electronic structure based approach, New PhaComp, provided much more accurate predictions of the observed σ phase formation in the CrMnFeCoNi$_x$ and CrMn$_x$FeCoNi systems and could be manipulated to obtain σ formation temperatures. As such, this method could be extremely useful to those wanting to design CrMnFeCoNi high entropy alloys that are free from the σ phase.

Keywords: High Entropy Alloys; phase diagrams; phase transitions; thermodynamic modeling

Introduction

The CrMnFeCoNi high entropy alloy (HEA), first proposed and discussed by Cantor *et al.* [1], has formed the basis of a number of studies on HEAs, many of which focus on understanding the phase equilibria and precipitation behaviour of the alloy [2-10]. It has now been conclusively established that a single, stable *fcc* (A1) solid solution phase exists at temperatures above 800˚C and up to the alloy melting temperature. However, phase equilibria studies at temperatures below 800˚C have revealed the formation of additional phases in the microstructure. Long duration exposures at 700˚C (up to 12000 hours), resulted in the formation of the topologically close packed (TCP) sigma (σ) phase [2-4], which is believed to be stable in the 480 – 800˚C temperature range. Exposures at 500˚C, identified the formation of the tetragonal (L1$_0$) NiMn phase, an ordered B2 FeCo phase, as well as the precipitation of a second solid solution phase based on Cr with a *bcc* (A2) structure [3,4]. Furthermore, the formation of carbides and ceramic inclusions has also been reported at various temperatures, which are believed to be a result of impurities incorporated into the material during processing [2,11,12].

In the context of evaluating HEAs for engineering applications at elevated temperatures, the nature of the precipitating phases is of critical importance to the viability of the alloys. In particular, TCP phases such as the σ phase, cannot be tolerated in the microstructure as they lead to a deterioration of the mechanical properties of the material [13-16]. Therefore, understanding the origins of σ phase precipitation is key in order to achieve the required balance of properties necessary for engineering applications [17]. However, this endeavour is further complicated by the inherent nature of the σ phase. Whilst the phase is routinely observed in structural metallic systems incorporating Cr additions, such as Ni-based superalloys and stainless steels, its chemical composition is known to vary from system-to-system

[13,18,19]. Crystallographically, the phase consists of close packed atomic layers separated from each other by large interatomic distances and arranged in a body centred tetragonal structure, which is responsible for the embrittling nature of the phase [13,18,19]. Generally, it is believed to form with the A_xB_y formula, in which x and y are approximately equal [18,19]. In structural metallics, Cr has been identified as the major σ forming element, and is found in the phase in concentrations of ~ 50 at.%. Refractory elements, such as Mo and W are also known to play a key role on the stability of the phase [13].

One of the great challenges for the high entropy alloy community is to identify optimal alloy compositions for a certain set of targets. Given that these materials already have a high degree of compositional complexity, which becomes greatly exacerbated when considering variations away from equiatomic ratios, it's clear that computer guided design methods are essential [17,20-22]. In this regard, thermodynamic calculations based on the CALPHAD approach seem highly suitable, as large swathes of compositional space can be evaluated in a relatively short period of time. Indeed, several down-selection strategies based on this approach have been reported in the literature [17,20-22]. However, all of these methodologies rely on the accuracy of the thermodynamic data in the underlying databases and the efficacy of the energy minimisation processes. Consequently, for these approaches to be viable, their predictions must accurately reflect experimental observations and thus, it is critically important to compare these two types of data. It is also essential that validatory activities are not solely limited to higher temperatures, e.g. > 1000˚C, where solid solution phases are favoured.

In the CrMnFeCoNi system, thermodynamic predictions have been used to investigate the stability of the single *fcc* solid solution phase, particularly with respect to the σ phase. He *et al*. [9] used the CALPHAD approach to identify the limits of the stability of single phase solid solutions based on the CrFeCoNi system. These results, which were verified using experimental data of alloys exposed at 900˚C for 72 hours, illustrated that the concentration of Cr that may be tolerated in the alloys is lower than any of the other constituent elements. This point was further strengthened by Laurent-Brocq *et al*. [10] and Bracq *et* al. [8], in similar studies using CrMnFeCoNi as the base system. The addition of Mn has also been shown to play a key role in destabilising the single phase solid solution in favour of the σ phase. CALPHAD calculations have shown an expansion of the σ phase field with increasing concentration of Mn as well as an increase in the σ phase solvus temperature. Experimental studies of CrMnFeCoNi with varying Mn contents examined at temperatures between 500 – 1000˚C validated these general trends, but found that the σ phase stability was under predicted by the thermodynamic models [8,11].

Whilst the effects of Cr and Mn on promoting the formation of the σ phase are now well established, understanding the role that Ni, Co and Fe have on the stability of the single phase *fcc* solid solution is equally important in providing a holistic view of the CrMnFeCoNi system. He *et al.* [9], postulated that additions of Fe, Co and Ni of up to 40 at. % would stabilise the single *fcc* solid solution phase at 900˚C. In contrast, Bracq *et al.* [8] suggested that the stability of the *fcc* solid solution would increase with Ni and Co additions, but that increased concentrations of Fe destabilised the alloy towards the formation of intermetallic phases. Laurent-Brocq *et al.* [10], have shown experimentally that even relatively low concentrations of Ni promotes the formation of a single *fcc* phase in the $CrMnFeCoNi_x$ system. However, the phase formation was only considered following 6 hours at 1100˚C and no experimental data exists for thermal exposures at lower temperatures or longer durations, where the formation of the σ phase is more likely.

Consequently, further investigations are required to experimentally establish the role of Ni, Co and Fe on the stability of the single *fcc* phase in the CrMnFeCoNi system and understand the nature of the σ phase. To this end, herein we present a detailed microstructural analysis of three alloys within the $CrMnFeCoNi_x$ system, with x= 0, 0.5 and 1.5, which were homogenised just below their solidus temperatures prior to 1000 hour exposures at 700 and 900˚C. The experimental results were compared to thermodynamic predictions performed using ThermoCalc to assess the fidelity of the TCHEA1 database.

Experimental

Three alloys with nominal compositions of $CrMnFeCoNi_x$, x = 0, 0.5, 1.5, Table 1, were manufactured by arc melting under an Ar atmosphere from raw elements of at least 99.5 % purity. The ingots were inverted and re-melted five times in order to increase the macroscopic homogeneity of the cast material. Differential scanning calorimetry (DSC) measurements of the as-cast material were performed on a Netzsch DSC 404 instrument operated at heating/cooling rates of $10^{\circ}C.min^{-1}$. The results obtained were used to ensure that the homogenisation heat treatment temperatures chosen were below the alloy solidus temperatures. Alloys $CrMnFeCoNi_{0.5}$ and $CrMnFeCoNi_{1.5}$ were both heat treated at 1200˚C for 100 hours whereas, due to the presence of two melting events, alloy CrMnFeCo was heat treated at 1050˚C for 100 hours. Following the homogenisation heat treatments, samples from each alloy were thermally exposed at 700 and 900˚C for 1000 hours, as these temperatures were believed to bracket the σ solvus temperature. All heat treatments were performed in Ar-backfilled quartz tubes to limit the effects of oxidation and environmental attack on the material.

Specimens from each heat-treated condition were prepared for microstructural characterisation by grinding with progressive grades of SiC paper and polishing to a 0.06 µm finish using colloidal silica. Imaging and compositional characterisation was performed using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) on an FEI Nova NanoSEM equipped with a Bruker XFlash 6 solid-state detector. Additional phase characterisation of each heat-treated condition was performed using X-ray Diffraction (XRD) on a Bruker D8 Advance diffractometer using Ni-filtered Cu Kα radiation. Patterns were recorded in the 20-100˚ 2θ range at 0.02˚ increments and were analysed using the full-pattern Pawley fitting procedure [23] in TOPAS-academic.

Results

As-cast & Homogenised material

Understanding the transition temperatures, and in particular the liquidus and solidus temperatures of the alloys, was critical in determining suitable homogenisation heat treatments for each alloy. Therefore, the as-cast material was heated to 1400˚C in a DSC and the corresponding data are shown in Figure 1 and the key results summarised in Table 2. The liquidus temperature of the alloys studied was found to decrease from 1370˚C for the quaternary CrMnFeCo alloy to 1340˚C for both alloys containing Ni. Similarly, the solidus temperature of the Ni-containing alloys was found to marginally decrease for the alloy with a higher Ni concentration. The quaternary alloy, CrMnFeCo, displayed two melting events one beginning at ~ 1125˚C and another one at 1310˚C.

Backscattered electron images (BSE) of the three alloys examined following their respective homogenisation heat treatments are shown in Figure 2. Alloys $CrMnFeCoNi_{0.5}$ and $CrMnFeCoNi_{1.5}$ both displayed homogeneous microstructures consisting of large, single phase grains, as shown in Figure 2b & 2c. In contrast, in the quaternary alloy CrMnFeCo, Figure 2a, at least two phases were visible in the microstructure. This observation, in conjunction with the DSC results of the as-cast material, indicated that it was not possible to heat treat, and hence homogenise, this alloy in a single-phase field. The bulk compositions of the alloys obtained by averaging at least five large area EDX scans (500 µm × 500 µm) are given in Table 1. Alloys $CrMnFeCoNi_{0.5}$ and $CrMnFeCoNi_{1.5}$ were found to exhibit compositions with only ~ 1.0 at. % deviation from the nominal for each element, whereas, alloy CrMnFeCo was found to deviate by ~ 2.0 at. % on the concentration of Co, which was compensated across the remaining four elements. XRD patterns collected from the homogenised alloys are shown in Figure 3, along with the corresponding Pawley refinements. These results confirmed that alloys $CrMnFeCoNi_{0.5}$ and $CrMnFeCoNi_{1.5}$ consisted of a single phase *fcc* solid solution following homogenisation with a lattice parameter of 3.60 ± 0.01 Å for both alloys. Similarly, the XRD results obtained from alloy CrMnFeCo confirmed the presence of at least two phases; an *fcc* solid solution and a σ phase. A third phase was also believed to be present in the pattern, although identification of the phase could not be reliably achieved from the diffraction peaks available as a result of the pattern being dominated by signal from the *fcc* and σ phases.

Long duration exposures

The propensity of the $CrMnFeCoNi_x$ alloys to form the σ phase was assessed following prolonged exposures at 700 and 900˚C using SEM/EDX analysis. This was supplemented by XRD for phase identification and determination of the associated lattice parameters. Figure 4 shows the collective SEM/EDX results from all alloys examined following 1000 hours at 900˚C. The CrMnFeCo alloy, Figure 4, displayed a microstructure consisting of a Co-Fe based matrix and bright, Cr-rich islands. Analysis of the XRD patterns, Figure 5, confirmed the presence of an *fcc* phase with a refined lattice parameter of 3.59 ± 0.01 Å, and the σ phase, with refined lattice parameters of a = 8.79 ± 0.01 Å and c = 4.56 ± 0.01 Å. In addition to the *fcc* matrix (dark contrast) and the σ phase (globular morphology, bright contrast), a fine, lenticular phase was also observed within the Co-Fe based matrix. Further examination of the BSE images and rigorous analysis of the XRD data, shown in Figure 6, indicated that this was the *hcp* allotrope of Co, with lattice parameters of a = 2.54 ± 0.01 Å and c = 4.10 ± 0.01 Å.

The $CrMnFeCoNi_{0.5}$ alloy exhibited large matrix grains and a bright Cr-rich phase precipitating both along the grain boundaries and intragranularly, Figure 4. The associated XRD patterns, Figure 5, indicated the presence of an *fcc* phase with a lattice parameter of 3.60 ± 0.01 Å, as well as peaks typical of the σ phase in the 40 – 60˚ 2θ range, giving refined lattice parameters of a = 8.81 ± 0.01 Å and c = 4.55 ± 0.01 Å. Compositional data obtained via EDX from the Cr-rich phase are given in Table 3, and are typical of the σ phase in this system [11]. Hence, the inter- and intragranular precipitates are the σ phase, which reside in an *fcc* multi-component matrix.

In contrast, no evidence of precipitates were observed either within the grains or along the grain boundaries of the $CrMnFeCoNi_{1.5}$ alloy Figure 4. Similarly, there were no variations in the corresponding elemental distribution maps, suggesting the alloy existed as a single solid solution phase. The XRD data contained reflections consistent with a single *fcc* structure that had a refined lattice parameter of 3.60 ± 0.01 Å. Consequently, at this temperature, this alloy was believed to be stable as a single solid solution phase.

Samples exposed at 700˚C for 1000 hours were examined in a similar manner, with the SEM/EDX data presented in Figure 7, and the XRD data shown in Figure 8. As with the sample exposed at 900˚C, the microstructure of the CrMnFeCo alloy following exposure at 700˚C contained a Cr-rich phase in an FeCo-based matrix, Figure 7. Fine, lenticular features were once again observed, identical to those shown in Figure 6. The XRD data indicated three phases corresponding to an *fcc* phase (a = 3.59 ± 0.01Å), an *hcp* phase (a = 2.55 ± 0.01 Å and c = 4.11 ± 0.01 Å) and the σ phase (a = 8.79 ± 0.01 Å and c = 4.55 ± 0.01 Å).

The microstructure of the $CrMnFeCoNi_{0.5}$ alloy, varied a little from that observed following the exposure at 900˚C. Cr-rich precipitates were observed to have formed along the grain boundaries, but there was no evidence of intragranular precipitation. The XRD data, shown in Figure 8, contained reflections consistent with an *fcc* phase (a = 3.59 ± 0.01 Å) and the σ phase (a = 8.80 ± 0.01 Å and c = 4.55 ± 0.01 Å). EDX data obtained from the Cr-rich phase indicated that it had a composition that was nearly identical to that obtained from the Cr-rich phase obtained from the sample exposed at 900˚C, Table 3.

Cr-rich precipitates were also observed decorating the grain boundaries of the $CrMnFeCoNi_{1.5}$ alloy following 1000 hours at 700˚C, Figure 8. However, these precipitates gave a darker BSE contrast in comparison to the matrix, unlike those observed in the $CrMnFeCoNi_{0.5}$ alloy, which gave a brighter contrast. This would suggest that these two phases are different; an observation supported by the notably different quantified compositions given in Table 3. The precipitates formed in the $CrMnFeCoNi_{1.5}$ alloy are significantly enriched in Cr and depleted in Mn, Fe and Co when compared to the σ phase observed in the $CrMnFeCoNi_{0.5}$ alloy. These elemental variations are not consistent with the expected composition of the σ phase and are far more in line with those of a carbide phase, as outlined in reference [11]. The XRD data for the $CrMnFeCoNi_{1.5}$ alloy , Figure 8, were also devoid of reflections typical of the σ phase but contained lower angle peaks, which aligned well with those expected from the cubic $M_{23}C_6$ phase. Again, this is in good agreement with previous studies in this system [2,3,11], however, additional site-specific characterisation would be required to conclusively establish the phase crystallography. It is worth noting that the peak present in some of the XRD patterns at an angle of ~ 29˚ was found to be an artefact from the diffractometer rather than being related to the samples being studied.

Discussion

The role of Ni on phase stability

Using the data presented above and results previously published in the literature for the equiatomic alloy CrMnFeCoNi [3,24], the role of Ni on the stability of the single phase *fcc* solid solution can be established. Ni is clearly a key stabilising element for the *fcc* phase, as demonstrated by the presence of multiple phases at all temperatures below the solidus in the quaternary CrMnFeCo alloy. Raising the Ni content to an atomic fraction of 0.5, or above, increases the relative stability of the *fcc* solid solution phase such that a single phase region exists below the solidus. The extent of this single phase field increases as a function of the Ni concentration with the formation of the σ phase depressed to progressively lower temperatures. For example, in the present work, the σ phase was observed at 900˚C in the CrMnFeCoNi$_{0.5}$ alloy, whereas in the equiatomic CrMnFeCoNi alloy the material retained a single *fcc* structure [3,24]. Similarly, the σ phase was observed in the equiatomic CrMnFeCoNi alloy following exposure at 700˚C, but the *fcc* phase of the CrMnFeCoNi$_{1.5}$ alloy remained stable. In an attempt to identify the σ solvus for each composition more accurately, samples of the exposed material that contained σ precipitates were studied using calorimetric methods. However, this proved unsuccessful as, with the exception of the quaternary CrMnFeCo alloy, the heat flow associated with the σ phase dissolution was too small for the solvus temperature to be reliably determined. This was most likely due to the low volume fraction of the σ phase in these alloys. For the quaternary alloy, where a clear signal was obtained, the onset of the σ phase dissolution was found to be ~ 1125˚C and corresponded to the incipient melting temperature.

Fidelity of thermodynamic predictions

A section of the pseudo-binary phase diagram between the quaternary CrMnFeCo alloy and Ni, predicted using the TCHEA1 database and ThermoCalc, is shown in Figure 9. These predictions suggest that there is a large single *fcc* phase field below the solidus, which is the only thermodynamically stable phase at temperatures above 500˚C when the concentration of Ni is greater than 32 at.%. With concentrations of Ni less than ~ 10 at.%, the thermodynamic predictions indicate that a *bcc* phase should also be present, which from the predicted molar fraction should constitute a significant proportion of the microstructure. The σ phase is also predicted to form at temperatures below 765˚C in the quaternary alloy and the formation temperature decreases progressively as the Ni content in the alloy increases.

When compared to the experimentally observed phases, the fidelity of these predictions is questionable. In the present study, no evidence of a *bcc* phase was found in any of the alloys, neither was any reported in the study by Bracq *et al.* [8]. However, in the quaternary alloy, the hexagonal ε allotrope of Co was identified in the experimental microstructures but was not predicted to form by the thermodynamic modelling. The predicted stability of the σ phase also deviated dramatically from what was observed experimentally. In the quaternary alloy, the σ phase was found to be present at all temperatures below the solidus. With increasing Ni content the formation temperature of the σ was observed to decrease but in all cases these temperatures were consistently higher than those predicted by ThermoCalc. To illustrate this point, the colour coded experimental data points have been overlaid on the phase diagram shown in Figure 9. The square green markers indicate a microstructure that is free from the σ phase and, therefore, barring impurity driven carbides, consist of a single solid solution phase. In contrast, the circular red markers indicate the presence of the σ phase, irrespective of whether it was observed intra- or intergranularly. The circular red points clearly demonstrate that the σ phase is much more prevalent than the thermodynamic simulations predict. This is consistent with previous similar comparisons of experimental and predicted phase stability in the CrMnFeCoNi system [8,9,11].

Alternative methods of predicting σ formation

Aside from thermodynamic calculations, electronic structure based methods, such as the Valence Electron Concentration (VEC) approach, have been proposed as potential alternatives for predicting phase stability [25]. This approach uses experimental observations to define certain empirical VEC ranges where different combinations of phases are stable. Whilst this approach does not provide reliable correlations over a wide range of different alloy systems, it can be informative within a single alloy family [26]. This concept has been extended specifically to predict the formation of the σ phase [27], where it has been suggested that if an alloy has a VEC value between 6.88 and 7.84 then it will be prone to σ phase formation at 700˚C.

The VEC numbers for the alloys in the CrMnFeCoNi$_x$ family, where *x* = 0, 0.5, 1, 1.5, are 7.50, 7.78, 8.00 and 8.18 respectively. As such, at 700˚C the VEC approach would predict that the alloys with Ni$_0$ and Ni$_{0.5}$ are prone to the formation of σ, whilst the equiatomic alloy and Ni$_{1.5}$ would be stable. This is in reasonable agreement with the experimental data, although the σ phase has been observed at this temperature in the equiatomic alloy [2,3]. However, the application of this approach is somewhat limited, as the critical VEC range when σ is likely to form will have a temperature dependence and hence a significant number of experimental data points would be required to define these critical ranges at multiple temperatures.

Another electronically based approach to predicting phase stability is the calculation of average d-orbital energies. These averaged energies correlate well with the atomic misfit and electronegativity of the alloy and, therefore, are a parametric representation of the Hume-Rothery rules [28-32]. The average d-orbital energy, $\overline{M}_d$ is calculated using the following expression where X_i is the atomic concentration and $M_{d,i}$ the d-orbital energy of the *i*th element.

$$\overline{M}_d = \sum_{i=1}^{n} X_i M_{d,i}$$

The use of average d-orbital energy has previously been used to consider TCP formation in HEAs [33,34]. When considering the wide range of different alloys assessed, the magnitude of the average d-orbital energy at which the σ phase was observed varied quite significantly [33,34]. Thus, it is not possible to define a general criterion and the crystal structure of the solid phase may also have an effect [34]. However, in nearly all of the different systems studied, the σ phase was found to form at higher average d-orbital energies. Again, as with the VEC ranges discussed above, these critical average d-orbital energies are likely to exhibit a temperature dependence, which will need to be taken into account if more reliable predictions are to be made.

An alternative way of utilising average d-orbital energies in *fcc* crystals is the New PhaComp method [28], which was originally developed to predict the occurrence of TCP phases in Ni-based superalloys [28,35,36]. Since the majority of the HEAs in the CrMnFeCoNi$_x$ family exist as a single *fcc* solid solution phase at temperatures close to the solidus, the New PhaComp approach may be suitable for predicting the formation of the σ phase in these alloys.

In contrast to the methods outlined above, the New PhaComp method incorporates a temperature dependence to the critical average d-orbital energy above which the formation of the σ phase is likely to occur. The formulation of this expression is shown below, where *T* is the absolute temperature and the two numerical constants are those empirically determined for Ni-based superalloys.

$$\overline{M}_{d,crit} = 6.25 \times 10^{-5} T + 0.834$$

Critically, this expression allows the formation temperature of the σ phase to be assessed as a function of composition by calculating the temperature at which $\overline{M}_{d,crit} = \overline{M}_d$. Following this approach for the current set of alloys, the variation in the σ formation temperature as a function of composition has been overlaid as a dotted line on the pseudo-binary phase diagram shown in Figure 9. As can be seen, this line correctly describes the presence of the σ phase in all but one condition, the CrMnFeCoNi alloy at 700˚C. However, it should be noted that the construction of the pseudo-binary phase diagram necessitates the used of nominal compositions, where Cr, Mn, Fe and Co must be present in equiatomic concentrations. Clearly, this is unlikely to be the case in real alloys. Consequently, if the σ formation temperature is recalculated using the actual compositions then the experimentally observed behaviour in the CrMnFeCoNi$_x$ system is accurately captured.

A similar outcome is reached if the phase equilibria of alloys with varying Mn content, i.e. CrMn$_x$FeCoNi, are considered in the same way. Experimental data has shown that whilst the equiatomic alloy is prone to the formation of the σ phase, decreasing the Mn content stabilises the *fcc* solid solution phase [11]. Thermodynamic calculations predict the formation of the σ phase at 600˚C for Mn concentrations between 0 and ~85 at.%, which does not align with the experimental observations. In contrast, New PhaComp approach correctly predicts the change in σ formation behaviour. This suggests, that within the CrMnFeCoNi system, this simple method may enable a rapid assessment of the likelihood of σ phase formation.

Furthermore, it should be noted that the current predictions of the σ formation temperatures are based upon numerical constants that have been empirically determined for Ni-based superalloys. It is not clear that these constants are directly applicable to HEAs and, as such, it may be appropriate to optimise these values for a given HEA system if sufficient data is available as to the role of each constituent element. However, at present, insufficient data relating to the influence of each elemental species on the formation of the σ phase within the CrMnFeCoNi system exists to perform such an optimisation. In particular, more data is required with respect to the influence of Fe and Co on σ phase formation. Critically, it is clear that current, widely used, thermodynamic databases do not have sufficient accuracy in CrMnFeCoNi-based HEAs to provide predictions with the fidelity necessary for alloy design and their use in this regard requires caution.

Conclusions

This study has experimentally investigated the role of Ni concentration on the stability of the single solid solution phase in the CrMnFeCoNi$_x$ family of HEAs and has assessed the fidelity of current thermodynamic methods for predicting the formation of the σ phase.

Ni has been shown to be a strong *fcc* stabiliser, supporting the stability of the single solid solution phase and suppressing the formation of the Cr-rich σ phase. Without Ni, the CrMnFeCo quaternary alloy formed the σ phase from the liquid, whereas the CrMnFeCoNi$_{1.5}$ alloy was found to be a single solid solution phase at temperatures above 700˚C. The σ phase was found to form in alloys with intermediate Ni compositions but its solvus temperature progressively decreased as the Ni concentration increased.

Thermodynamic predictions of this system provide a poor description of the observed phases. This is especially true at low Ni concentrations, where a *bcc* phase is predicted to form in significant fractions but was not found in any of the experimental data. Consequently, at present, care should be taken when considering the outputs of such models in the CrMnFeCoNi HEA system.

The formation of the σ phase can also be predicted using methods based on the electronic structure of the material. The New PhaComp approach can be manipulated to provide a σ formation temperature based on two empirical constants. This method was found to accurately capture the formation of the σ phase in both the CrMnFeCoNi$_x$ and CrMn$_x$FeCoNi systems, even when using the empirical constants determined for Ni-base superalloys. As such, with further optimisation, it is believed that this approach may be extremely useful as a simple predictive tool to assess the likelihood of σ phase formation in the CrMnFeCoNi system.

Acknowledgements

HJS and NGJ would like to acknowledge the support of the EPSRC/Rolls-Royce Strategic Partnership under EP/M005607/1.

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Table 1: Nominal and actual compositions obtained through large area EDX analysis (at. %).

Alloy	Composition (at. %)	Cr	Mn	Fe	Co	Ni
CrMnFeCo	nominal	25.0	25.0	25.0	25.0	-
	actual	23.7 ± 0.5	23.2 ± 0.5	25.7 ± 0.5	27.4 ± 0.5	-
CrMnFeCoNi$_{0.5}$	nominal	22.2	22.2	22.2	22.2	11.1
	actual	21.8 ± 0.2	21.5 ± 0.2	22.5 ± 0.2	23.2 ± 0.2	11.0 ± 0.2
CrMnFeCoNi$_{1.5}$	nominal	18.2	18.2	18.2	18.2	27.3
	actual	18.8 ± 1.0	18.1 ± 1.0	19.0 ± 1.0	17.6 ± 3.0	26.5 ± 1.0

Table 2: DSC results of the as-cast material.

Alloy	Liquidus (˚C)	Solidus (˚C)
CrMnFeCo	1370	1310 / 1125
CrMnFeCoNi$_{0.5}$	1340	1283
CrMnFeCoNi$_{1.5}$	1340	1267

Table 3: Composition of Cr-rich phases in alloys CrMnFeCoNi$_{0.5}$ and CrMnFeCoNi$_{1.5}$ obtained through spot EDX analysis.

Alloy	Condition	Cr (at. %)	Mn (at. %)	Fe (at. %)	Co (at. %)	Ni (at. %)
CrMnFeCoNi$_{0.5}$	900˚C / 1000 hours	37.9 ± 0.2	17.5 ± 0.1	19.4 ± 0.1	20.0 ± 0.2	5.2 ± 0.1
	700˚C / 1000 hours	38.9 ± 1.7	16.8 ± 0.6	18.6 ± 0.4	20.8 ± 0.3	4.9 ± 0.5
CrMnFeCoNi$_{1.5}$	700˚C / 1000 hours	72.3 ± 5.9	7.7 ± 1.2	7.3 ± 1.2	5.5 ± 1.4	7.2 ± 2.0

Figure 1: Differential Scanning Calorimeter thermograms of the as-cast alloys upon heating.

Figure 2: Backscattered electron images of the homogenised material a) CrMnFeCo following 100 hours at 1050˚C, b) $\mathrm{CrMnFeCoNi_{0.5}}$ and c) $\mathrm{CrMnFeCoNi_{1.5}}$ following 100 hours at 1200˚C.

Figure 3: X-ray diffraction patterns obtained for the three alloys tested following homogenisation heat treatments.

Figure 4: BSE images and EDX compositional maps following 1000 hours at 900˚C of alloys CrMnFeCo, $\mathrm{CrMnFeCoNi_{0.5}}$ and $\mathrm{CrMnFeCoNi_{1.5}}$.

Figure 5: X-ray diffraction patterns obtained for the three alloys tested following 1000 hours at 900˚C.

Figure 6: BSE image and XRD analysis showing in greater detail the fine lenticular features found to precipitate within the *fcc* matrix in alloy CrMnFeCo following exposures at 900˚C for 1000 hours.

Figure 7: BSE images and EDX compositional maps following 1000 hours at 700˚C of alloys CrMnFeCo, $\mathrm{CrMnFeCoNi_{0.5}}$ and $\mathrm{CrMnFeCoNi_{1.5}}$.

Figure 8: X-ray diffraction patterns obtained for the three alloys tested following 1000 hours at 700˚C.

Figure 9: Thermodynamcially predicted pseudobinary phase diagram between CrMnFeCo and Ni, overlaid with experimental data points. Circular red data points indicate alloys that contained the σ phase, whilst square green data points indicate alloys that were σ free. The dashed line indicates the σ phase field boundary predicted using the New PhaComp method. It should be noted that this diagram requires the data to be plotted against nominal, rather than actual, alloy compositions.