



Precipitation in the equiatomic high-entropy alloy CrMnFeCoNi



E.J. Pickering*, R. Muñoz-Moreno, H.J. Stone, N.G. Jones

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

ARTICLE INFO

Article history:

Received 25 September 2015

Accepted 11 October 2015

Available online xxxx

Keywords:

High-entropy alloys

Thermal stability

Precipitation

Metallurgy

TEM

ABSTRACT

CrMnFeCoNi is widely considered to be an exemplar high-entropy alloy, which is stable as a single solid-solution phase at all temperatures below its melting point. Here, for the first time, the formation of two distinct types of Cr-rich precipitate in coarse-grained CrMnFeCoNi is reported following prolonged exposures at 700 °C. The precipitates were identified as $M_{23}C_6$ and the σ phase, and their formation in unworked material during heat treatments without an applied stress indicated that they are equilibrium phases. Therefore, CrMnFeCoNi can no longer be regarded as thermodynamically stable as a single phase at all temperatures below its solidus.

© 2015 Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

High entropy alloys (HEAs) provide a new approach to the design of metallic materials, in which alloys are based on multiple principal elements rather than just one [1]. Conventional wisdom would suggest that these materials should have microstructures containing a number of intermetallic phases, yet much of the literature published since their inception has reported a limited number of solid solution phases with simple crystal structures or their associated superlattices. It has been suggested that these compositionally-complex solid solutions are stabilised against the formation of intermetallic phases by their high configurational entropies.

The complicated arrangement of different atomic species in HEAs is thought to give rise to a number of key benefits when compared to conventional, single-element based alloys. These include a highly-distorted lattice, which strengthens the material by hindering dislocation glide, and slow diffusion kinetics, which further enhances the high temperature strength and structural stability of these alloys [1–5]. However, in the last few years, some of the underlying principles that govern HEA behaviour have been challenged. For instance, the dominance of configurational entropy in determining phase stability in a number of systems has been questioned [6–9], and experimental observations suggest that the diffusion kinetics in all HEAs are not necessarily sluggish [10,11].

The equiatomic CrMnFeCoNi alloy was one of the earliest reported HEAs [12] and is often cited as an exemplar of the underlying concepts outlined above. One reason for this is that the alloy is widely reported to be a single solid solution phase with a face-centred cubic (*fcc*) crystal structure at all temperatures below its solidus [3,8]. The majority of previous studies of the alloy have focussed on its mechanical properties and processing response [13–25], as recently reviewed by Gludovatz et al.

[26]. However, the thermal stability of the alloy has received somewhat less attention. This may be attributed to the established consensus that the *fcc* solid solution is stable until the onset of melting [8,27–30].

Recently, and in contrast to the historical literature, two studies have reported Cr-rich grain-boundary precipitates within the microstructure of CrMnFeCoNi [20,31]. In one study [31], Cr and Mn rich precipitates were observed in arc melted and rolled material following low strain rate creep tests at 800 °C. In the second study, additional phases were found in severely plastically deformed material following exposures at 700 and 750 °C for 1 h [20]. The morphology and backscattered electron contrast of these precipitates were markedly different between the two studies, but in neither case were the crystal structures determined. It should be noted that these phases were only observed in material that had been under stress or had nano-crystalline grains, and this has led to the suggestion that these factors were significant in their formation [20,31]. Whilst precipitation has not been reported to occur to date in coarse-grained material, the observation of these phases in stressed samples casts doubts over the underlying stability of the single solid solution [20].

In the present work, we report on the phase evolution of coarse-grained CrMnFeCoNi following long-term heat treatment at 700 °C. We show, for the first time, that two different Cr-rich phases can precipitate on the grain boundaries of this material in the unworked state, and fully characterise their crystal structures. These results alleviate any doubt about the identity of the grain-boundary precipitates present in this alloy, rebuff the suggestion that stress is required for their formation, and directly challenge the belief that this alloy is thermodynamically stable as a single solid solution phase at all temperatures below its solidus.

An ingot of CrMnFeCoNi weighing 50 g was prepared via arc melting in an inert atmosphere from elemental metals with purity $\geq 99.5\%$. To

* Corresponding author.

E-mail address: ejp57@cam.ac.uk (E.J. Pickering).

Table 1

Composition (at. %) of the alloy investigated, as measured using EDX analysis. The error shown is one standard deviation across the ten measurements made.

Cr	Mn	Fe	Co	Ni
20.98 ± 0.10	20.00 ± 0.12	20.41 ± 0.07	19.35 ± 0.06	19.26 ± 0.15

increase compositional homogeneity, the ingot was inverted and remelted five times. A 5 mm diameter disc, 1 mm thick, was cut from the as-cast material and heated from room temperature to 1450 °C at 10 °C min⁻¹ under flowing argon in a Netzch 404 differential-scanning calorimeter (DSC). The remaining as-cast ingot was heat treated for 100 h at 1240 °C, 30 °C below the solidus temperature determined from the DSC data, and water quenched. Four sections, approximately 10 mm long, were cut from the homogenised ingot, encapsulated in evacuated argon-backfilled quartz ampoules, and aged at 700 °C for 125, 250, 500 and 1000 h, before quenching in water.

Specimens for scanning-electron microscopy (SEM) were prepared using standard metallographic techniques prior to characterisation in an FEI Nova NanoSEM microscope. Back-scattered electron (BSE) images were obtained in this instrument, along with energy-dispersive X-ray (EDX) maps acquired using a Bruker XFlash 6|100 detector. Quantitative EDX measurements of the bulk composition of the alloy were carried out using a CamScan MX2600, equipped with an Oxford Instruments x-act detector. Ten large areas, measuring at least 500 × 500 μm, were sampled and, as shown in Table 1, the homogenised material was within 1 at.% of the nominal concentration for each element.

Foils for transmission-electron microscopy (TEM) were extracted using focussed ion beam (FIB) milling in an FEI Nova 600 Nanolab Dual Beam microscope. Bright-field TEM images and electron diffraction patterns were acquired using an FEI Tecnai Osiris microscope operated at 200 kV.

The as-homogenised CrMnFeCoNi microstructure comprised a single solid solution with coarse grains and no evidence of secondary phases on grain boundaries or triple points, Fig. 1. EDX maps confirmed that the material was chemically homogeneous, apart from the presence of small oxide particles rich in Mn and Cr that were distributed throughout the material (not shown in Fig. 1). Such oxide particles have often been observed in arc-melted CrMnFeCoNi [8,14,19,24,29,31] and their presence can be attributed to contamination of the starting materials and melting apparatus.

Two sets of precipitates were observed in the material after heat treatment at 700 °C. The first of these decorated grain boundaries in every aged sample and appeared dark relative to the matrix in back-

scattered electron images, Fig. 2. EDX maps showed that these particles were enriched in Cr and depleted in the other alloying elements relative to the matrix. Selected-area electron diffraction patterns (SADPs), Fig. 2, revealed that the crystal structure of these precipitates was *fcc*, with a lattice parameter of approximately 10.6 Å, consistent with M₂₃C₆. The appearance and chemical composition of this phase matches the grain-boundary precipitates observed by He et al. [31], although they did not characterise the crystallography of the phase. The presence of a carbon-containing phase is almost certainly due to the contamination of the melting equipment and the starting elements from which the alloy was fabricated.

The second grain-boundary phase was observed in samples heat treated for 500 h and 1000 h, with the volume fraction increasing with exposure time. This phase appeared bright in BSE imaging, Fig. 3. EDX mapping indicated it was significantly enriched in Cr, and also contained some Mn, Fe and Co, but very little Ni. From SADPs, Fig. 3, the crystal structure was found to be tetragonal, with lattice parameters of *a* ≈ 8.8 Å and *c* ≈ 4.5 Å, consistent with the σ phase. The volume fraction of this phase was always found to be less than that of the M₂₃C₆. The appearance and chemical composition of these precipitates is consistent with the grain-boundary phase observed recently by Schuh et al. [20]. The apparent absence of M₂₃C₆ in their work can be attributed to the removal of carbon from the alloy through surface decontamination of Mn immediately prior to melting [16].

In the present work, the two precipitating phases were often observed to occupy the same grain boundary, but were very rarely found to be in contact. This suggests that the two phases formed independently and, therefore, were in direct competition for the available Cr. On this basis, it would be expected that the volume fraction of the σ phase should increase if the formation of M₂₃C₆ was suppressed. Indeed, the high volume fraction of σ phase observed in CrMnFeCoNi by Schuh et al. [20] following short exposures at 700 and 750 °C can be rationalised in this way, whilst also acknowledging the enhanced nucleation and growth kinetics expected in materials subjected to severe plastic deformation prior to heat treatment.

The presence of precipitates in coarse-grained CrMnFeCoNi, which had not been previously deformed and which was not subjected to an applied stress during exposure, strongly suggests that they are equilibrium phases at 700 °C. This observation is in direct contrast to the widely held belief that this alloy is thermodynamically stable as a single solid solution at all temperatures below its solidus. The majority of previous studies have utilised high-temperature heat treatments, often above 1000 °C [8,27–30], which are expected to be above the solvus temperatures of phases such as σ . In addition, the exposure times

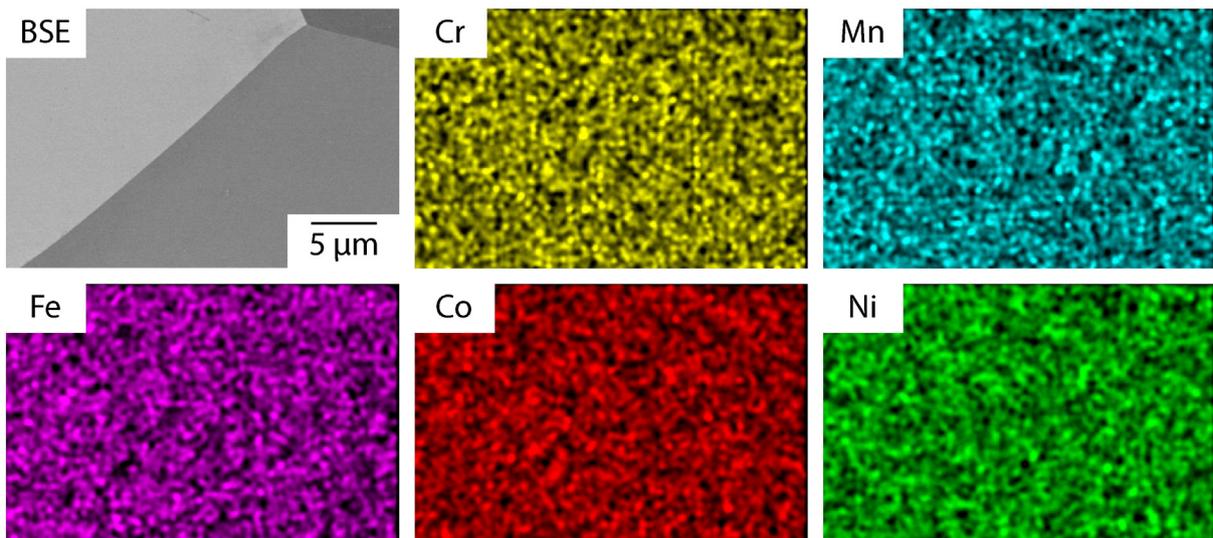


Fig. 1. BSE image and EDX maps of CrMnFeCoNi after homogenisation at 1240 °C for 100 h.

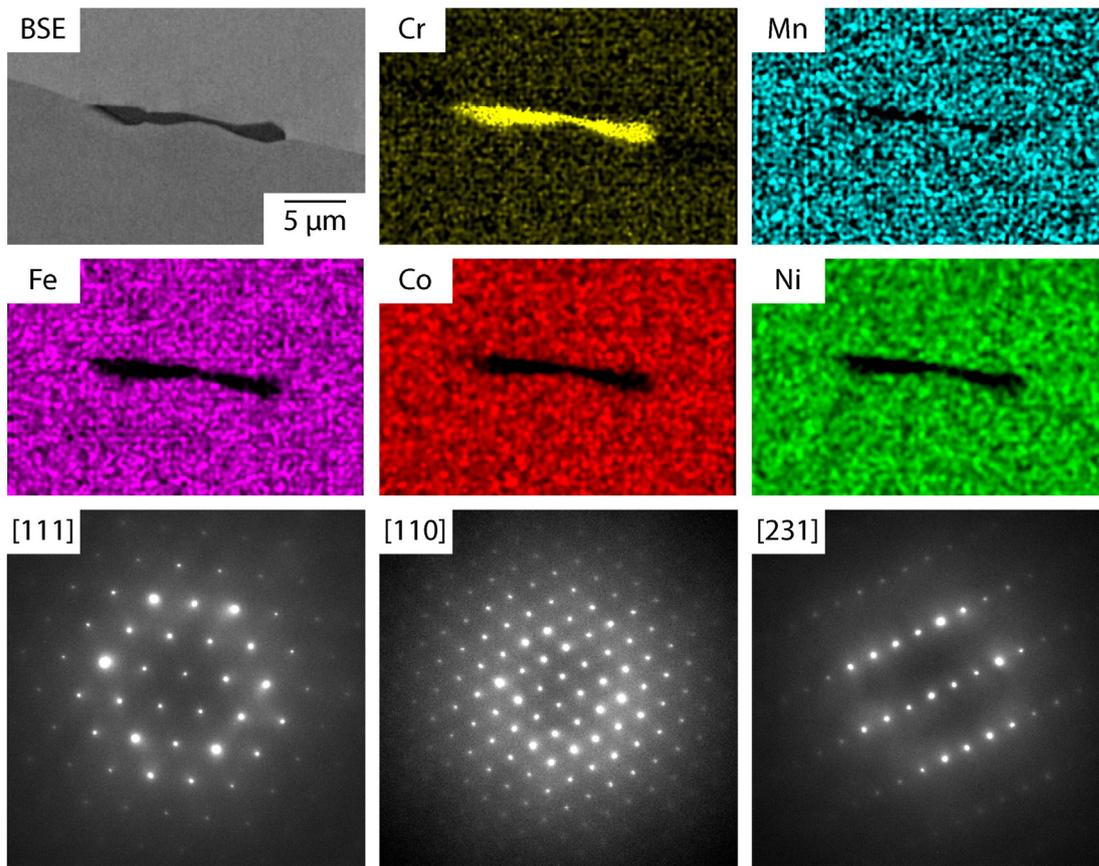


Fig. 2. BSE image, EDX maps and SADPs from the grain boundary precipitate that appeared dark in BSE imaging in CrMnFeCoNi homogenised and then heat treated for 1000 h at 700 °C.

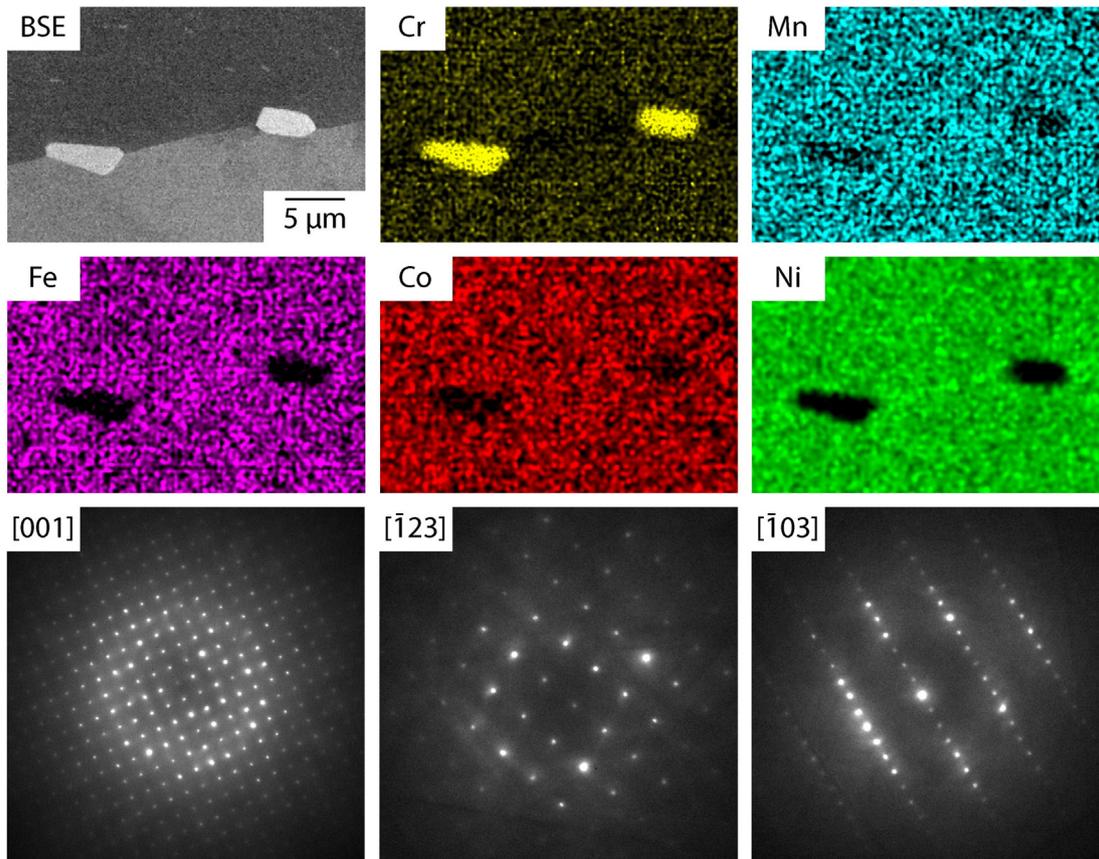


Fig. 3. BSE image, EDX maps and SADPs from the grain boundary precipitate that appeared bright in BSE imaging in CrMnFeCoNi homogenised and then heat treated for 1000 h at 700 °C.

used in these studies were all less than 100 h, which may not have been sufficient to allow secondary phases to form. These points were acknowledged recently by Laurent-Brocq et al. [30] and Schuh et al. [20], and the results of the present study simply prove their validity. The results also highlight that care must be taken when assessing the stability of these materials, as prolonged exposure times may be required before an equilibrium state can be reached. This is especially true in alloys that are believed to have sluggish diffusion kinetics.

In summary, this study has characterised the phase evolution of coarse-grained CrMnFeCoNi following prolonged exposure at 700 °C. It has been shown, for the first time, that two Cr-rich precipitates can form on the grain boundaries of this material through heat treatment alone. The two precipitates have been fully characterised using electron microscopy and identified as an $M_{23}C_6$ carbide and the topologically close packed σ phase. The observation of these phases in material that had not been deformed, nor exposed under an applied stress, indicates that the precipitates are equilibrium phases at 700 °C and do not require prior work or stress to form. As a result, the previous belief that CrMnFeCoNi is thermodynamically stable as a single solid solution at all temperatures below its solidus can no longer be considered valid.

Acknowledgements

The authors would like to thank K. Roberts and S. Rhodes for their assistance, and A.S. Wilson for helpful discussions. The authors acknowledge funding from the Rolls-Royce/EPSCRC Strategic Partnership (EP/M005607/1). The underlying data from this work can be found at the University of Cambridge data repository: <https://www.repository.cam.ac.uk/handle/1810/252342>.

References

- [1] J.-W. Yeh, S.-K. Chen, S.-J. Lin, J.-Y. Gan, T.-S. Chin, T.-T. Shun, C.-H. Tsau, S.-Y. Chang, *Adv. Eng. Mater.* 6 (2004) 299–303.
- [2] J.-W. Yeh, *Ann. Chimie Sci. Materiaux* 31 (2006) 633–648.
- [3] K.-Y. Tsai, M.-H. Tsai, J.-W. Yeh, *Acta Mater.* 61 (2013) 4887–4897.
- [4] M.-H. Tsai, J.-W. Yeh, *Mater. Res. Lett.* 2 (2014) 107–123.
- [5] J.-W. Yeh, *JOM* 67 (2015) 2254–2261.
- [6] N. Jones, J. Aveson, A. Bhowmik, B. Conduit, H. Stone, *Intermetallics* 54 (2014) 148–153.
- [7] O. Senkov, J. Miller, D. Miracle, C. Woodward, *Nat. Commun.* 6 (2015).
- [8] F. Otto, Y. Yang, H. Bei, E. George, *Acta Mater.* 61 (2013) 2628–2638.
- [9] D. Ma, B. Grabowski, F. Körmann, J. Neugebauer, D. Raabe, *Acta Mater.* 100 (2015) 90–97.
- [10] N. Jones, K. Christofidou, H. Stone, *Mater. Sci. Technol.* 31 (2015) 1171–1177.
- [11] E. Pickering, H. Stone, N. Jones, *Mater. Sci. Eng. A* 645 (2015) 65–71.
- [12] B. Cantor, I. Chang, P. Knight, A. Vincent, *Mater. Sci. Eng. A* 375–377 (2004) 213–218.
- [13] W. Liu, Y. Wu, J. He, T. Nieh, Z. Lu, *Scr. Mater.* 68 (2013) 526–529.
- [14] A. Gali, E. George, *Intermetallics* 39 (2013) 74–78.
- [15] C. Zhu, Z. Lu, T. Nieh, *Acta Mater.* 61 (2013) 2993–3001.
- [16] F. Otto, A. Dlouhy, C. Somsen, H. Bei, G. Eggeler, E. George, *Acta Mater.* 61 (2013) 5743–5755.
- [17] F. Otto, N. Hanold, E. George, *Intermetallics* 54 (2014) 39–48.
- [18] P. Bhattacharjee, G. Sathiaraj, M. Zaid, J. Gatti, C. Lee, C.-W. Tsai, J.-W. Yeh, *J. Alloys Compd.* 587 (2014) 544–552.
- [19] B. Gludovatz, A. Hohenwarter, D. Catoor, E. Chang, E. George, R. Ritchie, *Science* 345 (2014) 1153–1158.
- [20] B. Schuh, F. Mendez-Martin, B. Volker, E. George, H. Clemens, R. Pippan, A. Hohenwarter, *Acta Mater.* 96 (2015) 258–268.
- [21] N. Stepanov, M. Tikhonovsky, N. Yurchenko, D. Zybakin, M. Klimova, S. Zhrebtsov, A. Efimov, G. Salishchev, *Intermetallics* 59 (2015) 8–17.
- [22] W. Ji, W. Wang, H. Wang, J. Zhang, Y. Wang, F. Zhang, Z. Fu, *Intermetallics* 56 (2015) 24–27.
- [23] G. Laplanche, P. Gadaud, O. Horst, F. Otto, G. Eggeler, E. George, *J. Alloys Compd.* 623 (2015 a) 348–353.
- [24] G. Laplanche, O. Horst, F. Otto, G. Eggeler, E. George, *J. Alloys Compd.* 647 (2015 b) 548–557.
- [25] G. Sathiaraj, P. Bhattacharjee, *J. Alloys Compd.* 647 (2015) 82–96.
- [26] B. Gludovatz, E. George, R. Ritchie, *JOM* 67 (2015) 2262–2270.
- [27] G. Salishchev, M. Tikhonovsky, D. Shaysultanov, N. Stepanov, A. Kuznetsov, I. Kolodiy, A. Tortika, O. Senkov, *J. Alloys Compd.* 591 (2014) 11–21.
- [28] C. Tasan, Y. Deng, K. Pradeep, M. Yao, H. Springer, D. Raabe, *JOM* 66 (2014) 1993–2001.
- [29] N. Stepanov, D. Shaysultanov, G. Salishchev, M. Tikhonovsky, E. Oleynik, A. Tortika, O. Senkov, *J. Alloys Compd.* 628 (2015) 170–185.
- [30] M. Laurent-Brocq, A. Akhatova, L. Perriere, S. Chebini, X. Sauvage, E. Leroy, Y. Champion, *Acta Mater.* 88 (2015) 355–365.
- [31] J. He, C. Zhu, D. Zhou, W. Liu, T. Nieh, Z. Lu, *Intermetallics* 55 (2014) 9–14.