

Relative effects of enthalpy and entropy on the phase stability of equiatomic high-entropy alloys

F. Otto^{a,b,*}, Y. Yang^a, H. Bei^a, E.P. George^{a,b}

^a Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

^b Materials Science and Engineering Department, University of Tennessee, Knoxville, TN 37996, USA

Received 13 November 2012; received in revised form 11 January 2013; accepted 21 January 2013

Abstract

High configurational entropies have been hypothesized to stabilize solid solutions in equiatomic, multi-element alloys which have attracted much attention recently as “high-entropy” alloys with potentially interesting properties. To evaluate the usefulness of configurational entropy as a predictor of single-phase (solid solution) stability, we prepared five new equiatomic, quinary alloys by replacing individual elements one at a time in a CoCrFeMnNi alloy that was previously shown to be single-phase [1]. An implicit assumption here is that, if any one element is replaced by another, while keeping the total number of elements constant, the configurational entropy of the alloy is unchanged; therefore, the new alloys should also be single-phase. Additionally, the substitute elements that we chose, Ti for Co, Mo or V for Cr, V for Fe, and Cu for Ni, had the same room temperature crystal structure and comparable size/electronegativity as the elements being replaced to maximize solid solubility consistent with the Hume–Rothery rules. For comparison, the base CoCrFeMnNi alloy was also prepared. After three-day anneals at elevated temperatures, multiple phases were observed in all but the base CoCrFeMnNi alloy, suggesting that, by itself, configurational entropy is generally not able to override the competing driving forces that also govern phase stability. Thermodynamic analyses were carried out for each of the constituent binaries in the investigated alloys (Co–Cr, Fe–Ni, Mo–Mn, etc.). Our experimental results combined with the thermodynamic analyses suggest that, in general, enthalpy and non-configurational entropy have greater influences on phase stability in equiatomic, multi-component alloys. Only when the alloy microstructure is a single-phase, approximately ideal solid solution does the contribution of configurational entropy to the total Gibbs free energy become dominant. Thus, high configurational entropy provides a way to rationalize, after the fact, why a solid solution forms (if it forms), but it is not a useful *a priori* predictor of which of the so-called high-entropy alloys will form thermodynamically stable single-phase solid solutions.

© 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: High-entropy alloys; Multi-component alloys; Solid solution; Thermodynamics

1. Introduction

Metallic multi-component alloys containing four or more elements in equiatomic concentrations and referred to as high-entropy alloys, are currently receiving significant attention from the scientific community. Most such alloys are multi-phase alloys [2–5], but occasionally there have been reports of single-phase (i.e. solid solution) high-entropy alloys [1,6,7]. Cantor et al. [1] were the first to

report that an equiatomic alloy consisting of the five transition metals Co, Cr, Fe, Mn and Ni crystallized as a single solid solution phase (although these authors referred to their alloy as a multi-component alloy, not as a high-entropy alloy). From a metallurgical standpoint, the suppression of intermetallic phases in such an alloy, which consists of several disparate elements, is intriguing. In their pure form, these five elements have four different crystal structures at room temperature: Co is hexagonal close-packed (hcp), Cr and Fe are body-centered cubic (bcc), Mn has the *A12* structure (Pearson symbol cI58) and Ni is face-centered cubic (fcc). Nevertheless, Cantor et al. [1] showed that a simple dendritic microstructure, containing

* Corresponding author at: Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. Tel.: +1 865 574 6917; fax: +1 865 576 6298.

E-mail address: frederik.otto@rub.de (F. Otto).

no precipitates, formed after induction melting. Although some variations in the chemical compositions between dendritic and interdendritic regions were observed, an almost identical fcc crystal structure was found in both regions. These results contradict the usual observation that the highest mutual solubilities are found among atomic species that have the same crystal structure [8].

Yeh et al. [9] reasoned that the high configurational entropy of alloys containing multiple elements would be sufficient to thermodynamically stabilize a single-phase solid solution *via* a reduction of the Gibbs free energy. This led them to propose a new class of materials with potentially beneficial properties, the so-called high-entropy alloys, consisting of at least five elements, with atomic concentrations between 5 and 35%, that are solid solutions. Clearly, the equiatomic CoCrFeMnNi alloy of Cantor et al. [1] fits this definition. However, Cantor et al. had also demonstrated that simply increasing the system complexity (i.e. increasing the number of alloying elements) did not significantly extend single-phase stability in multi-component alloys. As an extreme case, they produced an alloy containing 20 elements (including non-transition and semi-metals) in equiatomic proportions, among them Co, Cr, Fe, Mn and Ni. Assuming ideal mixing, such an alloy has a significantly greater configurational entropy than the five-element CoCrFeMnNi alloy, but it nevertheless resulted in a brittle multi-phase microstructure [1]. Interestingly, Cantor et al. found that the primary fcc solid solution phase in the 20-element alloy was “particularly rich in transition metals, notably Cr, Mn, Fe, Co and Ni”. That is, despite the presence of multiple other alloying elements, the solid solution phase nevertheless consisted principally of their original five elements. This suggests that other factors, such as good chemical compatibility among the elements Co, Cr, Fe, Mn and Ni, are more important in determining the microstructural state than configurational entropy.

In spite of the above results of Cantor et al. [1] results, phase formation in multi-component alloys is often discussed in the literature on the basis of a high configurational entropy and the concomitant relaxation of the Hume–Rothery rules. As most of the investigated alloys contain at least three or four of the elements that were also present in Cantor’s CoCrFeMnNi alloy, it is not surprising that microstructures consisting predominantly of fcc solid solution phases of these elements were frequently obtained [2,10,11]. However, they also exhibited spinodal decomposition [2,10] and/or the presence of ordered phases/particles [2,11], and were not true single-phase microstructures.

To obtain a better understanding of the various factors that affect phase stability in high-entropy alloys, we undertook the present investigation to determine what happens when different elements are substituted one by one in the quinary CoCrFeMnNi alloy of Cantor et al. [1]. Our approach was predicated on the following premise: if any one element in Cantor’s alloy is replaced by another element while keeping the total number of elements constant, the configurational entropy of the alloy is, to first approx-

imation, unchanged. Therefore, if the magnitude of the configurational entropy is what determines single-phase stability in equiatomic multi-component alloys, as implied by Yeh et al. [9], each of our modified Cantor alloys should also exhibit single-phase solid solution microstructures, especially if the substitutional elements are similar to those that they replace in the sense of the Hume–Rothery rules.

To test this hypothesis, we started with the base CoCrFeMnNi alloy of Cantor et al. [1] and produced a series of equiatomic, quinary alloys by replacing the elements Co, Cr, Fe and Ni one at a time by 3d and 4d transition metals having the same room temperature crystal structure. In addition, the substitutional elements were chosen so as to match the replaced elements as closely as possible in terms of atomic radius and electronegativity. Our procedure resulted in the following five new equiatomic alloys, in which the substitutional element is italicized for ease of identification: CoCrFeMn*Cu*, *Ti*CrFeMnNi, Co*Mo*FeMnNi, Co*V*FeMnNi and CoCr*V*MnNi. In addition, we also produced the original CoCrFeMnNi alloy of Cantor et al. for comparison (this alloy is referred to as the “base alloy” in this paper).

As will be discussed in the body of the paper, each alloy underwent a three-day annealing treatment to ensure a near-equilibrium microstructural state. The resulting microstructures were investigated by means of scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). Thermodynamic calculations were performed to interpret the experimental observations and to determine the magnitudes of the driving forces responsible for phase stability in our equiatomic multi-component alloys.

For the readers’ convenience, the numerical values of the Pauling electronegativities EN [12] and atomic radii r_{atom} [13] for all elements considered in the present study are compiled in Table 1. In keeping with the Hume–Rothery rules, except for the element pair Ni–Ti, the differences in the atomic radii of the constituent elements in each alloy were kept below 15% (as obtained using the relationship $|r_{\text{atom},i} - r_{\text{atom},j}|/0.5(r_{\text{atom},i} + r_{\text{atom},j})$) and based on the metallic atomic radii for a coordination number of 12, as given in Ref. [13]. The bottom line of Table 1 lists the average differences in electronegativities and atomic radii, which were obtained by simply averaging the absolute differences of all possible binary combinations in each alloy. It can be seen that both of these averaged quantities are lowest for the CoCrFeMn*Cu* alloy while the highest values are obtained for Co*Mo*FeMnNi and *Ti*CrFeMnNi. Thus, on the basis of the Hume–Rothery rules, the Cu-containing alloy is expected to be the most likely to form a single-phase solid solution compared to the other five alloys in Table 1.

2. Experimental methods and thermodynamic calculations

Small buttons of each alloy, with a target weight of 120 g, were produced by arc melting under pure Ar atmosphere, after which they were drop-cast into cylindrical

Table 1

Electronegativities on the Pauling scale (EN) [12] and metallic radii (r_{atom} in pm) for a coordination number of 12 in the pure metal state [13] for the elements used to produce the quinary alloys investigated in the present study. In the bottom line, average differences in electronegativity and atomic radii are given for each alloy.

Element	CoCrFeMnNi		CoCrFeMnCu		CoMoFeMnNi		TiCrFeMnNi		CoVFeMnNi		CoCrVMnNi	
	EN	r_{atom}	EN	r_{atom}	EN	r_{atom}	EN	r_{atom}	EN	r_{atom}	EN	r_{atom}
Co	1.88	125.2	1.88	125.2	1.88	125.2			1.88	125.2	1.88	125.2
Cr	1.66	128.2	1.66	128.2			1.66	128.2			1.66	128.2
Fe	1.83	127.4	1.83	127.4	1.83	127.4	1.83	127.4	1.83	127.4		
Mn	1.55	126.4	1.55	126.4	1.55	126.4	1.55	126.4	1.55	126.4	1.55	126.4
Ni	1.91	124.6			1.91	124.6	1.91	124.6	1.91	124.6	1.91	124.6
Cu			1.90	127.8								
Mo					2.16	140						
Ti							1.54	146.5				
V									1.63	134.6	1.63	134.6
Δ_{av}	0.188	1.88	0.184	1.48	0.26	6.6	0.204	9.0	0.194	4.44	0.194	4.6

copper molds measuring 12.7 mm in diameter and 76.2 mm in height. To compensate for the Mn loss by evaporation, which was about 1 wt.% from our experience, an additional 1 g of Mn was added to the charge per 100 g of alloy before arc-melting. The Ti-containing alloy could not be drop-cast, as the arc-melted button was very brittle and broke into pieces after solidification; therefore, it was analyzed in button form.

The drop-cast ingots were annealed for three days in evacuated quartz capsules in order to reach a near-equilibrium microstructural state. To avoid melting of potential low-melting phases/interdendritic regions in the as-cast alloys, the annealing temperatures were kept below the lowest endothermic peak observed during heating in a differential scanning calorimeter (DSC). Since the alloy containing Cu exhibited a peak at a relatively low temperature of ~ 1212 K, it was annealed at 1123 K for 3 days. The other five alloys were annealed at 1273 K for 3 days as all their DSC peaks were above this temperature.

Metallographic specimens were prepared from each alloy using standard techniques and examined in a JEOL 6500F scanning electron microscope (JEOL Ltd., Tokyo, Japan) equipped with a field emission gun operated at an acceleration voltage of 15 kV and an EDAX Apollo 40 silicon drift detector (EDAX, Mahwah, NJ, USA) for EDX. For crystallographic phase identification, XRD measurements were conducted to identify the phases present in each alloy using a Scintag DMC-008 diffractometer (Scintag Inc., Cupertino, CA, USA) operated at 40 kV.

Thermodynamic calculations were performed using the software Pandat Version 8 (CompuTherm LLC, Madison, WI, USA) and the thermodynamic database SGTE SSOL4 [14]. Further details of the calculations are given in Section 3.2.

3. Results and discussion

3.1. Microstructures and prevalent phases

Fig. 1 presents representative SEM micrographs of the as-polished microstructures of the annealed alloys imaged

with backscattered electrons. The corresponding XRD patterns are given in Fig. 2. For the sake of clarity, only those peaks that could be assigned to the solid solution phases are indicated in Fig. 2. Drastic differences can be seen in these figures with regard to the microstructures and prevalent phases in the different alloys.

The microstructure of the base CoCrFeMnNi alloy is shown in Fig. 1a. Large, elongated grains can be seen which result from the directional solidification during casting. As expected from what was previously reported by Cantor et al. [1], the microstructure consists of only one phase (the small dark particles are oxides resulting from the oxygen in the raw materials and possibly also from contamination during arc melting). The XRD pattern in Fig. 2a confirms that all the peaks can be assigned to a single phase with the fcc crystal structure.

When Ni is substituted by Cu, the multi-phase microstructure shown in Fig. 1b is obtained. The presence of two separate fcc phases and most likely some σ phase is indicated by the corresponding XRD pattern in Fig. 2b. Interestingly, EDX measurements on this alloy revealed that the brighter of the two phases in Fig. 1b consists mainly of Cu (74 at.%) and Mn (19 at.%), with the other elements present at concentrations of less than 3 at.% each. The X-ray peaks designated “fcc₂” are believed to belong to this phase since their 2θ angles are very close to those of pure Cu. EDX indicates that the other fcc phase (labeled “fcc₁”) contains very little Cu (less than 4 at.%). Thus, a clear tendency for phase separation is found in the CoCrFeMnCu alloy.

Fig. 1c shows the microstructure of the CoMoFeMnNi alloy. It consists of a bright needle-like second phase embedded in a dark matrix. The XRD pattern reveals strong peaks consistent with the μ phase and an fcc solid solution phase. The μ phase has been shown to exist in the binary Co–Mo and Fe–Mo phase diagrams, as well as in the ternary system of these three elements [15]. Thus, its presence in this quinary alloy seems reasonable and is supported by the fact that EDX measurements reveal Mo (~ 38 –40 at.%), Co (~ 20 –21 at.%), and Fe (~ 19 at.%) to be the main components in the bright phase. As a result, the darker fcc matrix phase is highly depleted in Mo (less than 6 at.%).

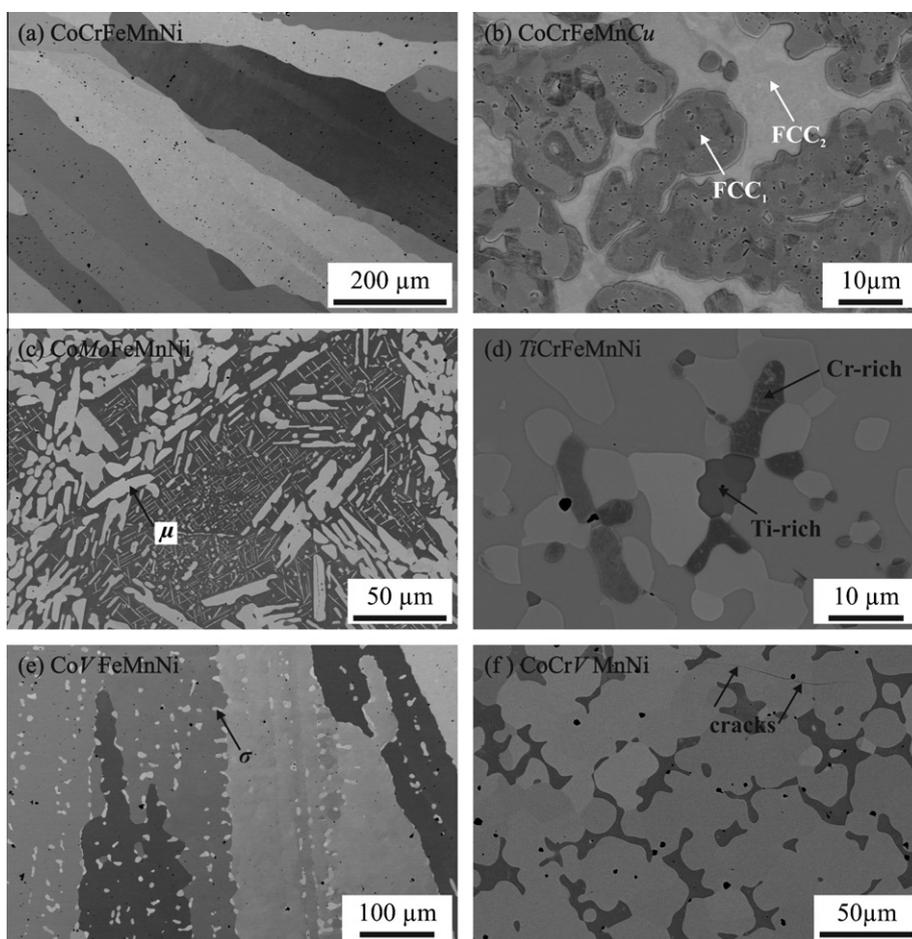


Fig. 1. Backscatter electron micrographs of the annealed microstructures of the six multi-component alloys investigated in the present study: (a) CoCrFeMnNi; (b) CoCrFeMnCu; (c) CoMoFeMnCu; (d) TiCrFeMnNi; (e) CoVFeMnNi; and (f) CoCrV MnNi. The small, dispersed dark spots in (a) are oxide particles (containing mainly Cr and Mn) resulting from trace levels of oxygen present in the raw materials and possibly also from contamination during arc melting.

In the Ti-containing alloy, the situation is complex. A careful examination of the microstructure reveals at least four different phases, as shown in Fig. 1d. Consistent with this, EDX showed that these phases had four distinctly different chemical compositions. The diffraction peaks in the XRD pattern in Fig. 2d exhibit a good match with the pattern of α -Mn. This suggests the presence of χ phase in our microstructure since the χ phase is isostructural with α -Mn [16] and it has been shown to exist in quaternary alloys containing Cr, Fe, Ni and Ti [17]. In addition, the small peaks at 2θ angles below 25° reveal the presence of an Fe₂Ti-type Laves phase which has been confirmed to exist in similar multi-component alloys that contain significant amounts of Ti [18,19]. Beyond this, it is difficult to say whether either of the two remaining phases is a solid solution phase due to the large number of peaks in the XRD spectrum. Recent reports from equiatomic, hexanary multi-component alloys that also contain Cr, Fe, Ni and Ti demonstrate that major fcc [18] or bcc [19] solid solution phases can be present, depending on which other alloying elements are also present. It is possible that both these solid solution phases are present in our alloy. For example, one

of our phases (highlighted by the arrow labeled Cr-rich in Fig. 1d), which is found to consist predominantly of Cr (~ 64 at.%), Fe (13 at.%) and Mn (16 at.%), is likely to be bcc according to the isothermal section of the Cr–Fe–Mn phase diagram at 1273 K [15]. However, from the EDX results, it is not possible to determine unambiguously whether an fcc solid solution phase is also present.

Fig. 1e shows the microstructure of the CoVFeMnNi alloy. The elongated grain structure bears a resemblance to that of the base CoCrFeMnNi alloy (Fig. 1a). However, a minor second phase can be seen in the interdendritic regions and at the grain boundaries. Because of its small volume fraction, the X-ray peaks corresponding to this second phase are small, but a careful analysis suggests that they are consistent with those of the σ phase. The appearance of σ phase in this alloy seems reasonable since the substitution of Cr with V leads to a wider region of σ phase stability in alloys containing Co, Fe and Mn [20]. Furthermore, V is the only element which forms the σ phase in combination with Ni [20], and EDX measurements reveal that the interdendritic/intergranular phase in Fig. 1e is indeed enriched in V, with a concentration of ~ 28 at.%.

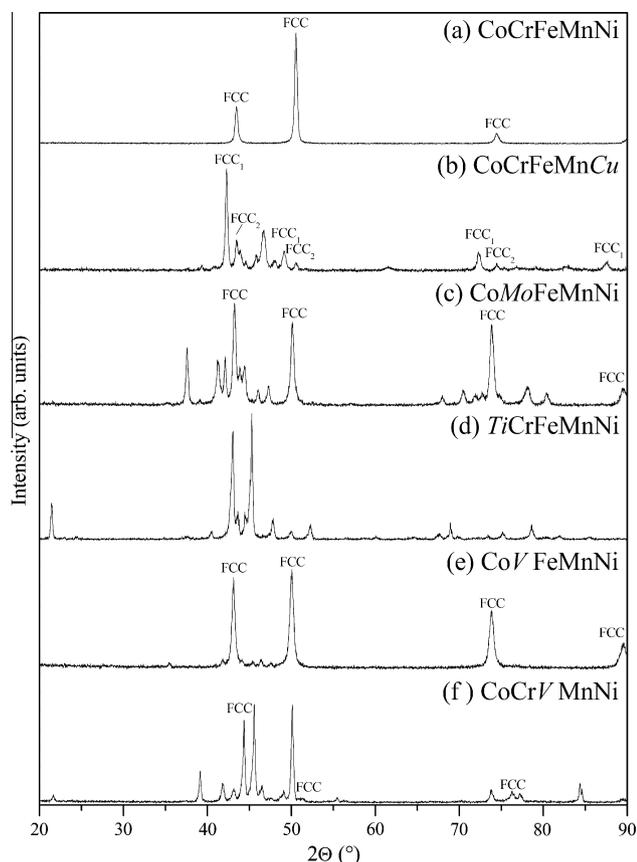


Fig. 2. X-ray diffraction patterns of the six alloys investigated in the present study after three-day anneals at 1123 K (spectrum b) and 1273 K (everything else).

The tendency of V-containing 3d transition metal multi-component alloys to form the σ phase is more obvious in the CoCrVMnNi alloy. Peaks can be observed in the XRD pattern in Fig. 2f corresponding to both an fcc solid solution phase and the σ phase. In the micrograph in Fig. 1f, cracks are visible in the brighter of the two phases (see arrows), which is likely the more brittle σ phase. The darker matrix between this brittle phase does not exhibit cracking. In fact, cracks appear to end at the interfaces between the two phases, suggesting that the dark matrix is the more ductile fcc solid solution phase.

Summarizing the microstructural results, we find that replacement of individual elements in an equiatomic, single-phase, high-entropy alloy can have profound effects on phase stability. We started with the quinary CoCrFeMnNi alloy of Cantor et al. [1], which exhibits a single-phase solid solution microstructure. In this base alloy, we replaced the elements Co, Cr, Fe and Ni one by one with the substitute elements Ti, Mo (or V), V and Cu, which at room temperature have crystal structures that are identical to those being replaced, along with similar atomic sizes and electronegativities. All six of the above alloys should therefore exhibit the same high configurational entropy if the various alloying elements are randomly distributed within each alloy. Nevertheless, a truly single-phase microstructure was obtained only in the base alloy. The five modified alloys either

contain multiple solid solution phases and/or a variety of topologically close-packed (tcp) phases, namely the σ , μ , χ and Laves phases. As tcp phases generally introduce some degree of ordering [16,20], the configurational entropy in such multi-phase alloys is different from that in a random solid solution phase. Therefore, the assumption that the substitution of one element with another while keeping the total number of elements the same leads to the same configurational entropy is not valid. It also calls into question the usefulness of configurational entropy as a reliable predictor of which equiatomic multi-element alloys will form true single-phase solid solutions. To better understand these issues, we next calculate the extent to which the thermodynamic properties that govern phase stability in our multi-component alloys deviate from those of an ideal random solid solution.

3.2. Thermodynamic analyses

Phase stability in alloys is governed by changes in the Gibbs free energy (G), which includes both enthalpy (H) and entropy (S) contributions. Here we are interested in the change in the Gibbs free energy of an alloy (ΔG) that arises from interactions between its individual constituents, such as mixing or the formation of intermetallic phases:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where ΔH and ΔS are the changes in enthalpy and entropy, respectively, and T is the temperature. In high-entropy alloys, solid solution phases are thought to be stabilized by their high configurational entropies [9]. In other words, their enthalpies of mixing as well as their non-configurational entropies of mixing are considered to be negligible, similar to the situation in an ideal solid solution (ISS), where these values are zero. In such cases, the change in the Gibbs free energy due to mixing, ΔG_{ISS} , is due only to the change in the configurational entropy:

$$\Delta G_{\text{ISS}} = RT \sum_{i=1}^n x_i \ln x_i \quad (2)$$

where R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and x_i is the concentration of component i in the mixture. For Eq. (2) to be valid in the case of any given multi-component alloy, the constituents would have to be such that they do not introduce significant enthalpy and non-configurational entropy contributions. In general, it would be rare to find four, five or more alloying elements that can fulfill this requirement in the so-called high-entropy alloys. Therefore, the more relevant question is: how far can the Gibbs free energy of the alloy deviate from that of an ideal solid solution and still result in a single-phase solid solution? If the Gibbs energy functions for the quinary systems of interest here were known, this question would be easy to answer. However, Gibbs energy functions for equiatomic compositions are generally available only for binary systems. Therefore, an alternative approach is taken here that involves pairwise analyses of the constituent binaries of our

quinary alloys to determine how far their thermodynamic properties deviate from those of an *ideal* fcc solid solution (as given by Eq. (2)) as well as from those of a *real* fcc solid solution (which is not necessarily an *ideal* solid solution). For the latter case, thermodynamic properties were calculated using the SSOL4 database [14] and the Calphad approach [21]. Through systematic comparisons, a better understanding is obtained of why phase stabilities in our six quinary alloys are so different even though they are all equiatomic and differ from each other in only one of their five constituent elements.

3.2.1. Ideal fcc solid solution vs. equilibrium state:

CoCrFeMnNi

The base solid solution alloy (CoCrFeMnNi) of Cantor et al. [1] is considered first. It contains ten binary pairs: Co–Cr, Co–Fe, Co–Mn, Co–Ni, Cr–Fe, Cr–Mn, Cr–Ni, Fe–Mn, Fe–Ni and Mn–Ni. For each of these binary systems, the enthalpy and entropy of mixing at the equiatomic composition were calculated. Calculations were performed at the two annealing temperatures used in this study (1123 K for CoCrFeMnCu and 1273 K for everything else). Since an fcc solid solution is the stable phase of the base alloy, the reference states of the constituent elements were chosen as pure metals with a (hypothetical) fcc crystal structure at either 1123 or 1273 K to facilitate comparison of the Gibbs free energies of the modified and base alloys. Enthalpy and entropy changes were calculated as the differences between the reference states and the equilibrium states of the equiatomic binary alloys, and the Gibbs free energy change in the system from Eq. (1). The equilibrium state represents the minimum energy state of the whole system, which can consist of non-ideal solid solution phases, intermetallic compounds, or a system consisting of both solid solution phases and intermetallic compounds. Therefore, the calculated ΔG , ΔH and ΔS are system values and not solely related to pure mixing effects; they can include energies of formation of second phases.

Next we define the thermodynamic quantities, H_D and S_D , which are the differences between the enthalpy and entropy values of the minimum-energy (equilibrium) state (Eq. (1)) and a hypothetical, ideal, solid solution state (Eq. (2)). In the case of the enthalpy term, H_D equals ΔH since there is no enthalpy term in Eq. (2). For the entropy term, we obtain:

$$S_D = \Delta S + R \sum_{i=1}^n x_i \ln x_i \quad (3)$$

Inserting $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and $x_i = 0.5$ for an equiatomic binary alloy, we get the following expression for the Gibbs free energy deviation from the ideal solid solution state:

$$G_D = H_D - TS_D = \Delta H - T\Delta S - 5.7628T \quad (4)$$

For a given binary system, if Eq. (4) yields values close to zero, it means that the Gibbs free energy of that system is close to that of an ideal solid solution.

The above approach is applied first to the single-phase CoCrFeMnNi alloy. Fig. 3a shows the entropy deviations of its constituent equiatomic binary pairs at 1123 K (triangles) and 1273 K (circles). By definition, at the zero line the mixing entropy is equal to that of an ideal solution. Although the product $T \cdot S_D$ has the dimensions of energy, we refer to it as the “entropy deviation” throughout this paper in order to clearly distinguish it from other energy contributions. As expected, Fig. 3a shows that the binaries in general are not perfect ideal solutions since entropy deviations from the zero line can be seen in all cases. However, at 1273 K, the entropy deviations are all within or close to $\pm 4 \text{ kJ mol}^{-1}$ except for Cr–Mn. Additionally, except for Co–Fe, which exhibits an entropy deviation of approximately 5.2 kJ mol^{-1} at 1123 K, the values of $T \cdot S_D$ are not strongly affected by the change in temperature. At 1273 K, we observe positive entropy deviations in six out of ten cases (five out of ten at 1123 K), which corresponds to absolute entropy values that *exceed* the configurational entropy of an ideal solid solution.

Fig. 3b plots the deviation of the enthalpy from an ideal solid solution state. Except for the systems Cr–Mn and Mn–Ni (and Co–Fe at the lower annealing temperature), the enthalpy deviations range within -4 to $+2 \text{ kJ mol}^{-1}$. The resulting values for the deviations in the Gibbs energy, which are obtained from Eq. (4), are depicted in Fig. 3c. With the exception of two binaries (Co–Mn and Mn–Ni), all values lie between -3 and $+0.5 \text{ kJ mol}^{-1}$, with no significant differences between the two temperatures at which the calculations were performed. In summary, the entropy/enthalpy/free energy values presented in Fig. 3 are all small and therefore the individual binary systems are expected to behave like ideal solid solutions.

In order to better understand the implications of Fig. 3 for phase stabilities, it is useful to relate them to the relevant microstructures. Table 2 compiles the equilibrium phases for each equiatomic binary system obtained from our thermodynamic calculations. These phase equilibria represent the lowest Gibbs free energy states of the equiatomic binary alloys, with the information in the upper right triangle of Table 2 corresponding to an annealing temperature of 1273 K and the lower left triangle (highlighted in grey) corresponding to a temperature of 1123 K. For the ten binary sub-systems of our CoCrFeMnNi alloy annealed at 1273 K, we obtain single-phase solid solution microstructures (having either an fcc or a bcc crystal structure) in eight out of ten cases (seven out of ten at 1123 K). The exceptions are the Co–Cr system, where the intermetallic σ phase is predicted, and Cr–Ni where a microstructure consisting of two solid solution phases with different crystal structures is predicted. At the lower temperature of 1123 K, an intermetallic phase with the stoichiometry Cr_3Mn_5 is predicted to be stable according to our calculations. However, as shown in Fig. 3, the Gibbs free energies of all these binaries are only slightly more negative than that of an ideal fcc solid solution. Therefore, in the quinary system composed of these binaries, these small energy

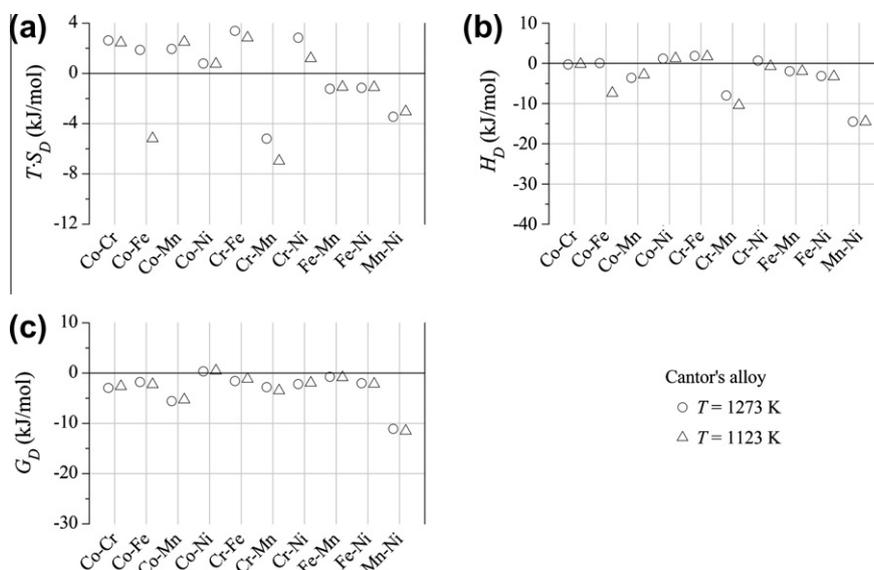


Fig. 3. Calculated deviations of (a) entropy, (b) enthalpy and (c) Gibbs free energy for all binary element pairs in the base CoCrFeMnNi alloy. The depicted values correspond to equiatomic alloys at 1123 K (triangles) and 1273 K (circles).

Table 2

Phase stabilities of equiatomic binary alloys calculated using the Calphad method. The information in the upper right triangle shows the stable phases predicted at 1273 K; the lower left region (highlighted in grey) lists the stable phases at 1123 K.

	Co	Cr	Fe	Mn	Ni	Mo	Ti	V
Co		FCC + σ	FCC	FCC	FCC	BCC + μ		σ
Cr	HCP + σ		BCC	BCC	FCC + BCC		BCC + Laves	BCC
Fe	BCC	BCC		FCC	FCC	BCC + μ	B2	σ
Mn	FCC	BCC + Cr ₃ Mn ₅	FCC		FCC	BCC + μ	BCC + Laves	BCC
Ni	FCC	FCC + BCC	FCC	FCC ^a		δ	B2	FCC + σ
Cu	2x FCC	FCC + BCC	2x FCC	FCC				

^a Phase diagrams show a B2 intermetallic compound here [15].

differences can be compensated for by the formation of an fcc solid solution with a higher configurational entropy (which is a natural outcome of increasing the number of elements to five in the quinary vs. two in the binaries). In other words, the thermodynamic properties of our base alloy are sufficiently close to those of an ideal fcc solid solution that configurational entropy is sufficient to overcome any tendency to form intermetallic or secondary solid solution phases.

The one exception to the above analysis is the Mn–Ni system, which exhibits relatively high deviations of entropy/enthalpy at 1273 K despite a single fcc solid solution phase being predicted to be stable. A possible explanation for this discrepancy is that the Gibbs energy functions of this binary system may not be described well in the available thermodynamic database due to the complexity and contradictions within the published Mn–Ni binary phase diagrams. Mn-containing systems are known to be difficult to model due to the large uncertainties in the experimental data (phase equilibria as well as thermodynamic properties). This is also manifested in the phases that are predicted to be stable in equilibrium. A single solid solution phase is

the only stable phase in the Mn–Ni system in Table 2, based on the SSOL4 database. However, the experimentally determined phase diagram includes an intermetallic B2 compound [15]. Therefore, the values for the Mn-containing binaries in Fig. 3 need to be interpreted with caution.

3.2.2. CoXFeMnNi ($X = Cr, Mo, V$)

Fig. 4 compiles values for the entropy and enthalpy, and the resulting deviations of the Gibbs free energy from the ideal solid solution state at 1273 K, for the two modified alloys in which Cr was substituted by either Mo (solid black symbols) or V (solid grey symbols). For ease of comparison, the values for the binary systems belonging to the base CoCrFeMnNi alloy (see Fig. 3) are also included (open symbols). Clearly, the substitution of Cr with either Mo or V leads to more negative entropy, enthalpy and free energy values. The exceptions to this general trend are binary combinations of these elements with Mn. Enthalpy deviations of the Mo-containing binaries range between -7.5 and -12.8 kJ mol⁻¹, and between -5.5 and -14.2 kJ mol⁻¹ for the V-containing binaries (Fig. 4b). Due to the decrease in entropy that is generally observed for the binary systems

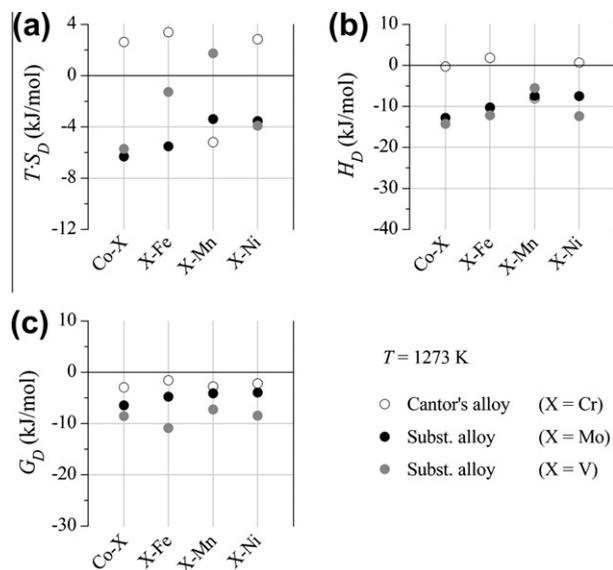


Fig. 4. Changes in the deviation of (a) entropy, (b) enthalpy and (c) Gibbs free energy for all binary element pairs as a result of replacing Cr in the base CoCrFeMnNi alloy (open symbols) with either Mo (black symbols) or V (grey symbols). The depicted values correspond to equiatomic alloys at 1273 K.

(Fig. 4a), their G_D values are slightly more positive than the aforementioned enthalpy deviations (see Eq. (4)). In all cases, G_D is the most negative for the V-containing binaries and closest to zero for the Cr-containing binaries (Fig. 4c).

As before, to put these thermodynamic properties into better perspective we relate them to the equilibrium phases present in the various binary systems shown in Table 2. Two-phase microstructures consisting of a bcc solid solution phase and the tcp μ phase can be seen for combinations of Mo with Co, Fe and Mn, while the equiatomic δ phase (Pearson symbol oP56) is stable in the Mo–Ni system at 1273 K. Microstructures consisting entirely of the σ phase are predicted to be stable for the binary systems Co–V and Fe–V, while a single-phase bcc solid solution is obtained for Mn–V. Ni and V form a two-phase microstructure consisting of an fcc solid solution and the σ phase. The presence of intermetallic compounds is reflected in the lower entropy values (stronger ordering) in combination with more negative enthalpy and Gibbs free energy values (Fig. 4). Note that the μ and σ phases, both of which are present in the binary systems containing Mo and V, are also found in our five-component modified alloys (see Figs. 1 and 2). That is, the trends observed in the binary systems are seen also in the multi-component quinary alloys.

3.2.3. CoCrXMnNi ($X = Fe, V$)

Fig. 5 shows that a replacement of Fe in the base CoCrFeMnNi alloy by V has a similar effect on the thermodynamic properties of the binary systems as a replacement of Cr by V. Again, except in the case of the Mn-containing binary systems, the substitution of Fe by V results in lower

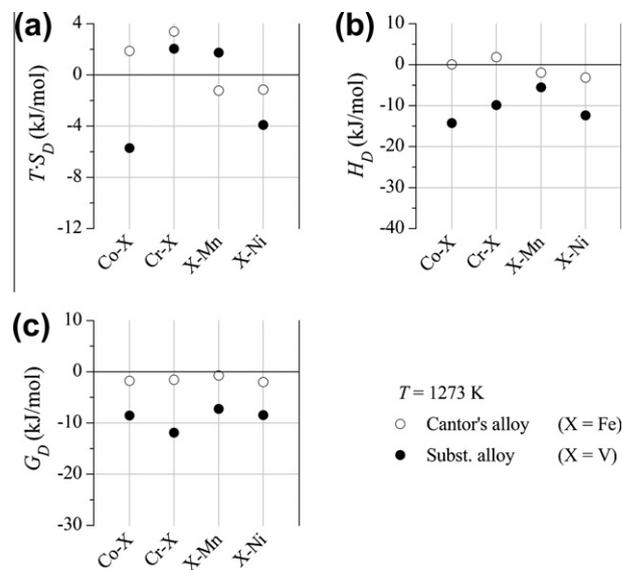


Fig. 5. Changes in the deviation of (a) entropy, (b) enthalpy and (c) Gibbs free energy for all binary element pairs as a result of replacing Fe in the base CoCrFeMnNi alloy (open symbols) with V (black symbols). The depicted values correspond to equiatomic alloys at 1273 K.

entropy, enthalpy and Gibbs free energy values, and thus more negative deviations from the ideal solid solution state. As already discussed in the previous section, the introduction of V generally results in an increased amount of σ phase (see Table 2). This corresponds well with the microstructure of our five-component alloy, where the σ phase is found to be abundant (see Figs. 1f and 2f).

3.2.4. XCrFeMnNi ($X = Co, Ti$)

The substitution of Co in the base CoCrFeMnNi alloy by Ti results in the most pronounced changes in entropy, enthalpy and Gibbs free energy, and, as shown in Fig. 6, the deviations of the Ti-containing binaries from the ideal solid solution state are the most severe. This is particularly true for the binary systems Fe–Ti and Ni–Ti, where strongly negative values can be found for $T \cdot S_D$, H_D and G_D . In these two cases, entropy deviations of -10 to -12 kJ mol $^{-1}$ and enthalpy deviations of -31 to -39 kJ mol $^{-1}$ were obtained from the calculations. The reason for this is the formation of equiatomic intermetallic B2 compounds (Table 2). In the systems Cr–Ti and Mn–Ti the formation of Laves phase is predicted together with bcc solid solution phases. On the basis of our XRD results (Fig. 2d), the Laves phase is indeed likely to be present. As already pointed out in Section 3.1, the presence of an intermetallic B2 compound could not be unequivocally confirmed by XRD, but its presence was suggested by EDX, which identified a phase containing about 48 at.% Ti along with substantial amounts of Fe and Ni.

3.2.5. CoCrFeMnX ($X = Ni, Cu$)

The replacement of Ni in the base CoCrFeMnNi alloy by Cu results in distinct differences in the thermodynamic properties of the binary systems compared to all of our other modified alloys. The calculated results shown in

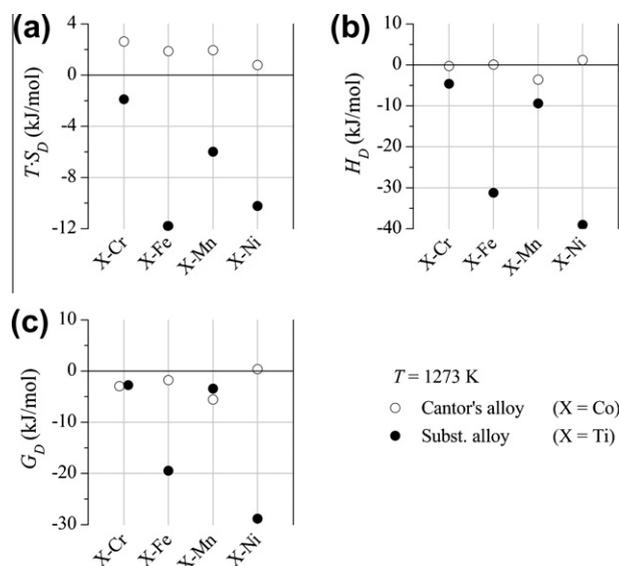


Fig. 6. Changes in the deviation of (a) entropy, (b) enthalpy and (c) Gibbs free energy for all binary element pairs as a result of replacing Co in the base CoCrFeMnNi alloy (open symbols) with Ti (black symbols). The depicted values correspond to equiatomic alloys at 1273 K.

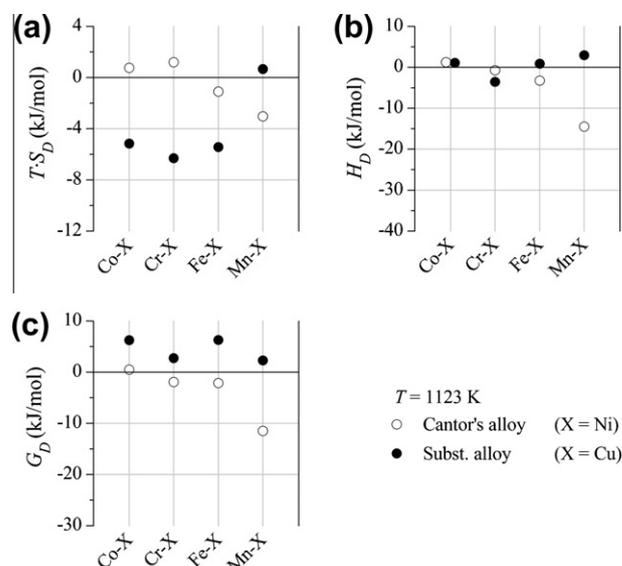


Fig. 7. Changes in the deviation of (a) entropy, (b) enthalpy and (c) Gibbs free energy for all binary element pairs as a result of replacing Ni in the base CoCrFeMnNi alloy (open symbols) with Cu (black symbols). The depicted values correspond to equiatomic alloys at 1123 K.

Fig. 7 were obtained at a temperature of 1123 K, which also leads to some changes in the behavior of the base alloy. Although one can again observe a decrease in entropy in three of four cases (Fig. 7a), the deviations of the Gibbs free energies from those of ideal binary solid solutions are *always* positive (Fig. 7c). For each of the other four substitutional alloys, the binary systems containing a substitutional element exhibited *exclusively* negative G_D -values (see Figs. 4–6). This is an important result, and is related to the different equilibrium microstructures in the binary systems that are formed when Ni is substituted by Cu. Table 2 shows that Cu does not form any stable intermetallic compounds, but tends to separate from Co, Cr and Fe, resulting in the formation of two solid solution phases. This phase separation is the result of the reduction in entropy, as can be seen from Fig. 7a. A single-phase fcc solid solution microstructure is only obtained in combination with Mn. These phase stability trends were also observed in our five-component CoCrFeMnCu alloy (Figs. 1b and 2b), where the solid solution phase designated “fcc₂” consisted almost exclusively of Cu and Mn while the other fcc solid solution phase (fcc₁) consisted of the remaining components. Therefore, analogous to what was observed in the other substitutional alloys, the phase stability trends in the binary systems carry over to the quinary alloy.

The presence of small amounts of σ phase, which was also observed in the CoCrFeMnCu alloy, must be interpreted as a result of the depletion/absence of the fcc solid solution stabilizers Mn and Ni and the concomitant shift in the relative concentrations of Cr, Co and Fe in the remaining phase.

3.2.6. fcc solid solution vs. equilibrium state

From Table 2 it can be seen that Cr does not form a single fcc solid solution phase in combination with any other element. This is partly due to the fact that Cr does not possess a stable fcc allotrope. The same can be said for V and Mo, which were used as substitutes for Cr. However, Cr forms an fcc solid solution phase when alloyed with four other elements in the base CoCrFeMnNi alloy, while V and Mo do not. This suggests that Cr might be more readily accommodated in the fcc crystal structure than the other two elements. A similar argument can be made for Ti, which substitutes for Co. Ni and Cu, on the other hand, exhibit only the fcc crystal structure. Nevertheless, Cu does not form a single solid solution phase when alloyed with Co, Cr, Fe and Mn, whereas Ni does. It is noteworthy that Cu and Ni themselves are completely miscible over a large temperature range. Our experimental results thus suggest that certain energy barriers can be overcome in multi-component alloys that indeed show a relatively high entropy, such as the base CoCrFeMnNi alloy (see Fig. 3a). However, an equally important conclusion from our study is that there are most likely only a few element combinations where this is possible.

In order to get a better idea of the relevant energy barriers, the Gibbs energy differences between the equilibrium states of our equiatomic binary systems (see Table 2) and their respective (possibly metastable) fcc single-phase solid solution states were calculated. The results are presented in Fig. 8. Fig. 8a compiles Gibbs free energy differences for the ten binary systems of the base CoCrFeMnNi alloy for the two temperatures at which calculations were performed. At a temperature of 1273 K, six out of ten data

points (five out of ten at 1123 K) show no difference in the Gibbs free energy between the fcc solid solution and the equilibrium state. This is because an fcc solid solution is the equilibrium state in these cases (see Table 2). As mentioned before, a single-phase fcc solid solution is never favorable for equiatomic binary systems containing Cr, which manifests itself in positive values in Fig. 8a. The slightly positive Gibbs energy difference that is observed for the equiatomic Co–Fe system at 1123 K is due to an fcc \rightarrow bcc phase transformation that occurs between the two annealing temperatures. In general, however, the values depicted in Fig. 8a are rather small, with the maximum Gibbs energy difference in the base CoCrFeMnNi alloy being less than 4 kJ mol⁻¹.

Fig. 8b–e illustrates the effect of element substitution in our alloys on the energy difference between an fcc solid solution and the equilibrium state. Element substitution leads to larger Gibbs energy barriers for the formation of single fcc solid solutions in almost all cases, with Cu–Mn being the only exception (Fig. 8e). When Cr is substituted in the base alloy by either Mo or V, the energy barrier to form the fcc solid solution is always the largest for Mo with

values of up to almost 7 kJ mol⁻¹. This might well be the reason for the larger phase fraction of the second phase observed in the CoMoFeMnNi alloy (Fig. 1c) compared to the CoVFeMnNi alloy (Fig. 1e). When Fe is substituted by V (Fig. 8c), the energy difference between an fcc solid solution and the equilibrium (bcc solid solution) state is even larger (approximately 8.6 kJ mol⁻¹). This shows the stabilizing effect of V on the bcc crystal structure. The highest overall changes in the Gibbs free energy differences are, however, observed when Co is substituted by Ti (Fig. 8d), with a maximum value of about 10 kJ mol⁻¹. This is the most likely reason for the lack of a major fcc solid solution phase in the microstructure of the TiCrFeMnNi alloy. Large energy barriers of more than 10 kJ mol⁻¹ can also be observed when Ni is substituted with Cu (Fig. 8e), although the latter element does not form intermetallic compounds with any one of the other constituents. This clearly shows the strongly repulsive interactions between Cu on the one hand and Co, Cr and Fe on the other, which leads to the formation of two separate fcc solid solution phases in the CoCrFeMnCu alloy.

4. Summary and conclusions

The goal of this study was to investigate how important a role configurational entropy plays in stabilizing single-phase solid solutions in equiatomic multicomponent alloys (the so-called high-entropy alloys). Our premise was that, if the elements in a single-phase solid solution high-entropy alloy are replaced individually by other similar elements, it should not change the configurational entropy; furthermore, if configurational entropy is in fact a dominant factor in phase stability, then the new alloys resulting from such a replacement should also be single-phase solid solutions. To this end, we started with the CoCrFeMnNi alloy of Cantor et al. [1], which is known to form a single-phase solid solution microstructure, and produced a series of equiatomic, quinary alloys in which the elements Co, Cr, Fe and Ni were substituted one by one by 3d or 4d transition metals with identical room temperature crystal structure and similar atomic radius and electronegativity. All the new substitutional alloys exhibited multi-phase microstructures containing intermetallic compounds and, in one case, two fcc solid solution phases. In order to rationalize the experimental observations, thermodynamic analyses were performed using the Calphad method. Together, the experimental results and the data obtained from the thermodynamic analyses allow further insight into the thermodynamic properties that govern phase stability in equiatomic multi-component alloys. Our findings can be summarized as follows:

- (1) In general, alloys consisting of five components in equiatomic concentrations do not exhibit a single-phase solid solution microstructure. In the present study, only one out of the six alloys investigated formed such a microstructure, despite the fact that

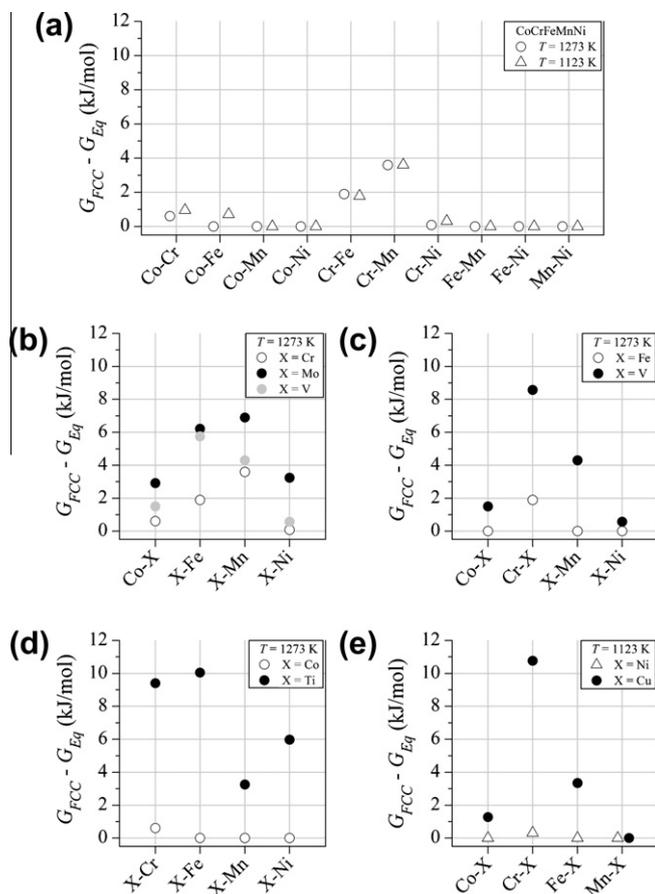


Fig. 8. Differences in the Gibbs free energies of (metastable) equiatomic, binary fcc solid solutions and their respective thermodynamic equilibrium states. (a) The base CoCrFeMnNi alloy at 1123 and 1273 K; (b–e) changes due to the substitution of (b) Cr with Mo or V, (c) Fe with V, (d) Co with Ti and (e) Ni with Cu.

only one element at a time was replaced and the substitutional elements were similar (in the sense of the Hume–Rothery rules) to those being replaced.

- (2) Phase formation in five-component (and possibly higher-order multinary) alloys is consistent with a minimization of the total Gibbs free energy, including both enthalpy and entropy contributions (and not just a maximization of the configurational entropy). In the equilibrium state, the Gibbs free energies of the ten binary pairs that make up the single-phase base CoCrFeMnNi alloy are close to that of an ideal solid solution. In the substitutional alloys, an energy reduction is achieved through precipitation of intermetallic compounds or the formation of separate solid solution phases.
- (3) Entropies can vary substantially in equiatomic, five-component alloys. On the basis of our thermodynamic calculations in binary systems, lower entropies can be expected for alloys exhibiting ordered phases or in which some kind of phase separation occurs. The highest entropy values are obtained in a true single-phase solid solution alloy, close to the theoretical configurational entropy of an ideal solid solution. Therefore, it makes sense to designate only true solid solution alloys, such as the CoCrFeMnNi alloy of Cantor et al. [1], as *high-entropy* alloys, while alloys that consist of multiple phases, which have lower entropies, are better referred to as multi-component alloys.
- (4) If an equiatomic, five-component alloy contains any elements that are prone to form phases with each other when alloyed as binary pairs, it is generally reflected in the microstructure of the five-component alloy as well. In the present study, this tendency was manifested in the precipitation of tcp phases or the formation of more than one solid solution phase. Thus a significant relaxation of the phase stability trends seen in binary systems due to possible entropy increases resulting from an increase in the number of alloying elements is not observed in higher-order systems.
- (5) Increased configurational entropy may stabilize single-phase solid solution microstructures in rare cases. Generally, however, this effect is insufficient to counteract the driving forces that favor the formation of secondary phases. This finding casts doubt on the usefulness of an alloying strategy that consists merely

of increasing the number of alloying elements if the ultimate goal is to produce a single-phase solid solution microstructure.

Acknowledgements

This research was supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. F.O. also received funding from the Alexander von Humboldt Foundation through a Feodor Lynen Research Fellowship.

References

- [1] Cantor B, Chang ITH, Knight P, Vincent AJB. *Mater Sci Eng A* 2004;375–377:213.
- [2] Tong CJ, Chen YL, Chen SK, Yeh JW, Shun TT, Tsau CH, et al. *Metall Mater Trans A* 2005;36:881.
- [3] Zhou YJ, Zhang Y, Wang YL, Chen GL. *Mater Sci Eng A* 2007;454–455:260.
- [4] Zhu JM, Fu HM, Zhang HF, Wang AM, Li H, Hu ZQ. *Mater Sci Eng A* 2010;527:7210.
- [5] Singh S, Wanderka N, Murty BS, Glatzel U, Banhart J. *Acta Mater* 2011;59:182.
- [6] Senkov ON, Wilks GB, Scott JM, Miracle DB. *Intermetallics* 2011;19:698.
- [7] Senkov ON, Scott JM, Senkova SV, Miracle DB, Woodward CF. *J Alloys Compd* 2011;509:6043.
- [8] Hume–Rothery W, Smallman RE, Haworth CW. *The structure of metals and alloys*. 5th ed. London: Metals & Metallurgy Trust; 1969.
- [9] Yeh JW, Chen SK, Lin SJ, Gan JY, Chin TS, Shun TT, et al. *Adv Eng Mater* 2004;6:299.
- [10] Chen MR, Lin SJ, Yeh JW, Chen SK, Huang YS, Chuang MH. *Metall Mater Trans A* 2006;37:1363.
- [11] Shun TT, Hung CH, Lee CF. *J Alloys Compd* 2010;493:105.
- [12] Allred AL. *J Inorg Nucl Chem* 1961;17:215.
- [13] Tilley RJD. *Understanding solids: the science of materials*. Hoboken, NJ: Wiley; 2004.
- [14] Scientific Group Thermodata Europe, SSOL4.9 (2004–2008): the SGTE general alloy solutions database, V4.9f.
- [15] Villars P, Okamoto H, Cenzual K, editors. *ASM alloy phase diagrams database*. Materials Park, OH: ASM International; 2006–2013. <<http://www1.asminternational.org/AsmEnterprise/APD>>.
- [16] Joubert JM, Phejar M. *Prog Mater Sci* 2009;54:945.
- [17] Hughes H, Llewelyn DT. *J Iron Steel Inst* 1959;192:170.
- [18] Zhou YJ, Zhang Y, Wang YL, Chen GL. *Appl Phys Lett* 2007;90:181904.
- [19] Wang XF, Zhang Y, Qiao Y, Chen GL. *Intermetallics* 2007;15:357.
- [20] Joubert JM. *Prog Mater Sci* 2008;53:528.
- [21] Kaufman L, Uhrenius B, Birnie D, Taylor K. *CALPHAD* 1984;8:25.