

# Faraday Discussions

Accepted Manuscript



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

This article can be cited before page numbers have been issued, to do this please use: B. Cantor, *Faraday Discuss.*, 2025, DOI: 10.1039/D5FD00110B.

Brian Cantor<sup>a,b</sup>

<sup>a</sup>Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK:  
[brian.cantor@materials.ox.ac.uk](mailto:brian.cantor@materials.ox.ac.uk)

<sup>b</sup>Brunel Advanced Solidification Centre (BCAST), Brunel University London,  
Uxbridge, UB8 3PH, UK; [brian.cantor@brunel.ac.uk](mailto:brian.cantor@brunel.ac.uk)

## Abstract

Multicomponent phase space is enormous and contains a vast number of complex new materials. Despite intensive investigation in the last decade and a half, however, we are only slowly making progress towards understanding these new materials. This paper attempts to summarise some of the fundamental discoveries we have made about the geography of multicomponent phase space and the wide range of complex new materials that we have found within it. It discusses briefly the following topics: the size and shape of multicomponent phase space and the range of single- and multiple-phase fields that it contains; the (initially) surprising presence of many large near-ideal single-phase solid-solution phases, stabilised by a high configurational entropy of mixing; the extensive and wide-ranging variation of local nanostructure and associated mechanical and electronic lattice strain that permeates throughout high-entropy solid-solution phases; and some of the unusual, exciting and valuable properties that are then produced within multicomponent and high-entropy materials. Many of the results discussed have been obtained from the fcc Cantor alloys (based on the original Cantor alloy, equiatomic fcc CrMnFeCoNi) and the bcc Senkov alloys (based on the original Senkov alloy, equiatomic VNbMoTaW), two groups of multicomponent high-entropy single-phase materials that have been particularly widely studied. Similar behaviour is also found in other multicomponent high-entropy single-phase materials, though these have not been studied so intensively. In comparison with multicomponent high-entropy single-phase materials, rather little is known about multicomponent multiphase materials that have also not been studied so intensively.

## Keywords

Multicomponent materials; high-entropy materials; Cantor alloys, Senkov alloys, nanostructure; atomic clusters; vacancies; diffusion; dislocations; slip; grain boundaries; recrystallisation; surfaces; catalysis



## 1. Introduction

View Article Online  
DOI: 10.1039/D5FD00110B

All materials are alloys<sup>\*</sup>.<sup>1,2</sup> This is sometimes for the negative reason that we can never manufacture perfectly pure materials without retaining small admixtures of impurities (a consequence of the third law of thermodynamics); but it is more often for the more positive reason that we frequently add alloying elements to obtain secondary properties in a material or to tweak the primary properties of its main component. Until recently almost all the materials we have made and used have been composed of one or occasionally two main components and a relatively small number of relatively low-level dilute alloying additions.<sup>1-3</sup> In 1979, I invented the concept of *multicomponent materials*<sup>†</sup>, i.e. materials with more (and often many more) than two components in relatively concentrated proportions,<sup>3-5</sup> and the first experiments to investigate multicomponent materials were performed in 1980 under my supervision by an undergraduate student, Alain Vincent, for his short 2<sup>nd</sup>-year undergraduate project at the University of Sussex.<sup>3-5</sup> These first experiments led almost immediately to the discovery of a number of interesting multicomponent materials including the first high-entropy material, the original Cantor alloy<sup>‡</sup>,

<sup>\*</sup> This paper uses the term *alloy* to mean any mixture of more than one starting material or component. The term alloy is used most commonly to refer to metallurgical materials, but here it is used more generally for any mixture of materials, whether metallurgical, ceramic, semiconductor, polymeric or of any other type. Since all materials are alloys, as explained in the main text, the two terms *material* and *alloy* are fairly synonymous but not entirely, since referring to different alloys usually means referring (only) to different compositions of the mixed components, whereas referring to different materials often means referring to different compositions but can also mean referring to the same composition made under different manufacturing conditions and with different resulting microstructures. Thus, for instance, martensitic and ferritic steels with the same composition are the same alloy but different materials; and, similarly, amorphous and devitrified soda-lime glasses with the same composition are also the same alloy but different materials.

<sup>†</sup> This paper draws a distinction between *multicomponent* and *high-entropy* materials. The term *multicomponent material* is taken to mean any material containing three or more components, i.e. with  $c \geq 3$  where  $c$  is the number of components in the material. This is logical and natural, in line with the normal definition of multiple as meaning more than one or two. The term *high-entropy material* is more restrictive and is taken to mean any multicomponent material, i.e. any material containing three or more components with  $c \geq 3$ , where in addition the components are all or almost all in one or, at most, two random or near-random solid-solution phases. This is again more logical and natural, in line with the implied normal definition of high entropy as meaning a configurational entropy of mixing in the material sufficiently large to stabilise one or at most two random solid-solution phases, rather than forming a mixture of several or many stoichiometric, fixed-composition or near-fixed-composition compounds. This is different, but simpler and less arbitrary, than the common usage of the terms *high-entropy material* and *medium-entropy material* to mean any material containing high concentrations of more than five components, i.e.  $c \geq 5$ , and between three and five components, i.e.  $5 \geq c \geq 3$  respectively. Overall the definitions used in this paper are, as already indicated, more logical and more natural than some common practice, and also more useful, since they carefully separate the different concepts of multiplicity of components and entropy in any given material.

<sup>‡</sup> The term *Cantor alloy* means any multicomponent material with a single-phase random or near-random solid-solution face-centred cubic (fcc) structure. There are very many Cantor alloys with different compositions, as discussed later in the main text.



consisting of five components (Cr, Mn, Fe, Co and Ni) in equal proportions, with a single-phase random solid-solution face-centred cubic (fcc) crystal structure, which can be represented more succinctly as fcc CrMnFeCoNi\*. These studies were reported in Vincent's undergraduate project dissertation<sup>5</sup> at the University of Sussex but, although the results were indisputable and very clear, they were not of the quality needed to be accepted by a research journal for publication. For complex reasons, it was a long time before the work could be repeated, so the results were not fully published until more than twenty years later. The multicomponent material concept was first published, therefore, in 2002 and 2003, when it was mentioned briefly in the introduction to several papers by myself with other colleagues on some multicomponent amorphous alloys,<sup>6-9</sup> work that was performed in the early 2000s, i.e. much later than the original work by Vincent. The original work was finally published in our seminal paper<sup>4</sup> expounding the details of the new concept in 2004. In the meantime, Jien-Wei Yeh in Taiwan had quite independently had similar ideas to me and had pursued similar experiments in the mid-1990s, and he and his colleagues had also discovered immediately a variety of interesting multicomponent materials that he at first called multiple principal-element materials. This work also took some time (though not quite so long) before it was finally published in four papers,<sup>10-13</sup> again in 2004. In one of them, another seminal paper<sup>11</sup> again expounding the details of the new concept, he invented the alternative name *high-entropy materials* that has been used widely (and somewhat confusingly, as explained in a previous footnote and in a later section) for the whole field of multicomponent materials.

There was antipathy and some disdain amongst scientific colleagues and research funders in the 1980s, 1990s and 2000s about the idea of investigating multicomponent and high-entropy materials, and Yeh and myself both received considerable resistance from our respective academic establishments against pursuing our early experiments, which partly explains the lengthy delays in both cases between our first research work being undertaken and then finally being published.<sup>14,15</sup> For similar reasons, our first published papers on multicomponent and high-entropy materials in the early 2000s, including the two seminal papers mentioned above, did not initially receive much (or even any) significant scientific

\* This paper adopts the convention of naming multicomponent and high-entropy materials by listing their components in ascending atomic number rather than alphabetically, i.e. the original Cantor alloy is represented as CrMnFeCoNi rather than CoCrFeMnNi. This has the advantage of emphasising more clearly the chemical nature of the different components. This paper also adopts the convention of naming multicomponent and high-entropy materials by using subscripts for the atomic percent rather than weight percent of the different components, but truncated by leaving out the subscripts when the components are present in equiatomic proportions, i.e. the original Cantor alloy is represented as CrMnFeCoNi, truncated from Cr<sub>20</sub>Mn<sub>20</sub>Fe<sub>20</sub>Co<sub>20</sub>Ni<sub>20</sub>. The paper deviates from the ascending atomic number convention when it contradicts a well-established usage. Thus the well-known and important ordered body-centred cubic (bcc) multicomponent monoaluminide is represented as (CrMnFeCoNi)Al rather than Al(CrMnFeCoNi).



attention, with only a few citations in the first five or ten years following their publication. Since then, however, scientific interest has mushroomed rapidly, with citations increasing dramatically and multi-million dollar research programmes being initiated in many countries worldwide.<sup>3,16,17</sup> The discovery of multicomponent high-entropy materials has opened up the possibility of developing many new materials with exciting new properties and, after an initial delay, scientists have, not surprisingly, begun to realise their potential and have been increasingly active in investigating different multicomponent materials and trying to understand their structures and properties.<sup>3,16</sup> The Web of Science gives a total up to the present time of almost fifty thousand research papers on multicomponent or high-entropy alloys or materials, and Google Scholar gives a total of approximately ten and fifteen thousand citations respectively for each of the two seminal papers by Cantor and Yeh mentioned above. And the number of scientific papers on multicomponent materials as well as the number of citations to them are both continuing to rise rapidly.

The last decade and a half in the 2010s and 2020s has seen, therefore, a fairly large body of scientific investigation into the manufacture and resulting structures and properties of multicomponent and high-entropy materials.<sup>3,16,17</sup> It turns out, however, that multicomponent phase space is vast, and contains a truly enormous number of materials, running into many trillions, the majority of which have still never been made let alone investigated in any detail.<sup>3,16,17</sup> Until we began to study multicomponent materials seriously in the 2010s and 2020s, virtually all the materials that we had ever made had been based, as mentioned above, on either a single component or binary mixtures of different components, with only occasionally a concentrated ternary addition, and with higher order (quaternary, quinary, etc.) additions never much above very dilute levels. To put it another way, all our materials have until recently been at or very close to the corners and binary edges and occasionally the ternary faces of multicomponent phase space, and we have until recently avoided exploring the inner regions within the main body of multicomponent phase space where most of the compositions of the trillions of different and new multicomponent materials can be found. Unfortunately, it also turns out that our thermodynamic, classical and quantum mechanical, and statistical theories of the structure and properties of materials have all been devised for relatively pure materials and/or simple mixtures with only one or two relatively dilute alloying additions that can then be treated as relatively small and independent linear perturbations of the properties of the main component in the material.<sup>3,18</sup> Because of the approximations required to make these theories tractable as well as the multiplicity of parameters needed to make calculations based on them, our fundamental theories are not easily extrapolated to the complexity of multicomponent materials, which often exhibit non-linear behaviour because of the interactions between multiple components in concentrated proportions.<sup>3,18</sup> This means that in order to explore multicomponent phase space and the different





materials within it, there is no real alternative to massive amounts of experimental investigation to provide new data that will ultimately allow us to develop more complex and more definitive theories of multicomponent material structures and properties. At present, however, the size of multicomponent phase space is so large that, despite intensive research over the last decade and a half, we have still explored only a small fraction of the totality of all possible materials that could be made, so we are still a long way from developing a detailed scientific understanding of the range and extent of all the different multicomponent materials and their structures and properties.<sup>3,18</sup>

View Article Online

DOI: 10.1039/D5FD00110B

Despite these difficulties, after considerable false starts and with considerable initial misunderstandings, we have finally begun to understand some of the main features of the geography of multicomponent phase space and of the structures and properties of some of the different multicomponent materials within it,<sup>3,16,17</sup> and it is the purpose of this paper to try to summarise briefly where we have got to. I do this by asking a series of simple and obvious questions (that I am frequently asked) and either giving the answer or answers that we have finally been able to come up with, often after a lot of hard work to clear away initial misconceptions, or alternatively indicating the extent of our continued lack of understanding and the need for further work (a conclusion that is still fairly common, essentially because of the enormity of multicomponent phase space and the complexity of the structure and properties of the multicomponent materials within it).

## 2. How many materials are there?

The number of materials we can make depends firstly on the number of starting materials or components  $c$  that we have available, and secondly on the material specification  $x$ , i.e. the difference in composition that separates two similar but different materials. For a material specification  $x$  in at% or mole%, there are  $n = 100/x$  different compositions available for each of the components in the material. The specification  $x$  is important<sup>19-21</sup> in defining the range of compositions within which a given material can vary and it can still be regarded as the same material with a specified structure and properties. The specification reflects the precision within which we can manufacture a material, as well as the precision we need for its application.<sup>19-21</sup> Anyone *making* a material needs to know how tight the composition must be controlled during manufacture, and anyone *using* a material needs to know that they have the correct material composition within this range and thus the correct specified properties. We can think of the totality of multicomponent phase space as being represented by a  $c$ -pointed hyperpolyhedron in  $(c - 1)$ -dimensional hyperspace with the number of different materials within it as being given by the number of composition points separated by  $x$  at% along each of the  $c$  polyhedral



View Article Online  
DOI: 10.1039/D5FD00110B

Open Access Article. Published on 09 September 2025. Downloaded on 9/11/2025 5:06:25 AM.  
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Faraday Discussions Accepted Manuscript











 non-metals	 main group metals	 actinides
 alkali metals	 semi-metals	 noble gases
 alkaline earths	 halides	
 transition metals	 lanthanides	

Figure 1: The periodic table.

We can generate the whole of multicomponent phase space, containing all the possible materials that could conceivably be made, by using all the elements in the periodic table, shown in Figure 1, as our set of starting materials or components. This gives us a total of  $c = 118$  components with which to manufacture different materials. We can reduce this to  $c = 80$ , by removing all the elements in row seven because they are radioactive with short lifetimes, and also removing all the elements in column eighteen because they are noble gases and chemically inert. Alternatively we might want to be more restrictive and take (say)  $c = 50$  or  $60$  because some of the remaining elements are highly reactive and difficult to handle, such as lithium, fluorine or arsenic, though all these elements are used in important materials. Most engineering materials are specified to  $x = 0.1\%$ , though lower-grade materials are often specified to no better than  $x = 1\%$  or  $5\%$ , and some high-performance materials require a greater degree of specification, down to  $x = 0.01\%$ , or  $0.001\%$ <sup>19-21</sup> (or even in some special cases to the nearest part per million (ppm) or  $x = 0.0001\%$ ).

		$c =$	40	50	60	70	80
$x$ (at%)	$n$						
5	20		16	18	19	21	22
1	$10^2$		36	41	46	50	53
0.1	$10^3$		72	86	100	111	123
0.01	$10^4$		111	134	157	179	200
0.001	$10^5$		150	183	216	248	279

Table 1: The number of different materials  $N$ , in the form  $\log_{10}(N)$ , that can be manufactured from  $c$  components, with a material specification of  $x$  at%, corresponding to a number of composition points  $n = 100/x$  for each component.

Table 1 shows the total number of materials that can be made using different assumptions for the number of components  $c$ , the specification  $x$ , and the number of composition points for each component  $n = 100/x$ . Taking  $c = 80$ ,  $x = 0.1\%$  and  $n = 1000$  gives the total number of materials that can be made as:

$$\ln N = 1079 \ln 1079 - 79 \ln 79 - 1000 \ln 1000 \approx 282$$

$$\therefore N = 10^{123}$$

Being extremely conservative and taking  $c = 60$  and  $x = 1\%$  or even  $5\%$  gives the total number of materials that can be made as  $N = 10^{46}$  or  $10^{19}$  respectively. In all cases, the number of possible materials that could be made is enormous. Many multicomponent material compositions will, of course, be difficult to manufacture and not be of much use. Nevertheless, it is quite clear that, whatever values are used





for  $c$ ,  $x$  and  $n$ , there is an extremely large number of different materials populating multicomponent phase space.

View Article Online

DOI: 10.1039/D5FD00110B

### 3. Are multicomponent materials the same as high-entropy materials?

The terms *multicomponent materials* (first used by me and my colleagues), *multiple principal-element materials*, and *high-entropy materials* (both first used by Yeh and colleagues) have often been used to mean the same thing.<sup>3,16,17</sup> This is misleading and somewhat confusing. I prefer to use *multicomponent materials* to mean all materials with more than one or two components, i.e. with  $c \geq 3$ ; *multiple principal-element materials* to mean all materials in which more than two of the components are in concentrated proportions<sup>\*</sup>; and *high-entropy materials* to mean all materials in which there is an entropy sufficiently high to favour the formation of one or at most two random or near-random solid-solution phases rather than a mixture of phases that are all pure or near-pure components and/or stoichiometric fixed-composition or near-fixed-composition compounds<sup>†</sup>. The three terms then neatly separate three different effects that can all be important independently in multicomponent materials, namely the *multiplicity* of the components, the *concentration* of the components, and the *high entropy* of mixing the components in a solid solution.<sup>3</sup> With these definitions, the set of multiple principal-element materials is a subset of the set of multicomponent materials (i.e. it excludes all *dilute* multicomponent materials), and the set of high-entropy materials is a subset of the set of multiple principal-element materials (i.e. it excludes all multicomponent materials where the configurational entropy is *not* decisive in stabilising one or at most two random solid-solution phases).

We have studied enough multicomponent materials to be able to say definitively that many but not all of them are high entropy materials.<sup>3,16</sup> In many cases, multicomponent materials have been found to exhibit no more than one or two random or near-random solid-solution phases:<sup>3,16,17</sup> in these cases, the configurational entropy of mixing is high enough to suppress chemical reactions between the

<sup>\*</sup> In this paper, the term *concentrated component* is taken to mean that a linear dilute solution approximation is not likely to be valid, i.e. that the different atoms of the component, when added in solution to the material, are not so widely separated that they can be treated as affecting the material independently or one at a time. In a solid or liquid material, atoms exhibit strong interactions chemically when they are first or second near neighbours, so a concentrated solute addition is typically above about one atom in twenty, i.e. >5%, depending somewhat on the structure of the host material.

<sup>†</sup> In this paper, the term *high entropy material* is taken to mean that the configurational entropy of the material is large enough to suppress or largely suppress the formation of stoichiometric fixed-composition compounds, leading instead to the formation of one or sometimes two extended solid-solution phases in which the atoms are randomly or near-randomly distributed across the lattice or sublattice points in the crystal structure of the material.



different components and the resulting formation of stoichiometric fixed-composition chemical compounds. These are high-entropy materials. In many other cases, however, multicomponent materials have been found to exhibit mixtures of multiple phases:<sup>3,16</sup> in these cases, the configurational entropy of mixing is not high enough to suppress chemical reactions between the different components and the resulting formation of stoichiometric fixed-composition chemical compounds. These are not high-entropy materials.

View Article Online  
DOI: 10.1039/D5FD00110B

#### 4. How many high-entropy materials are there?

As explained in the last section, not all multicomponent materials are high-entropy materials, although many are. In fact, we have studied enough multicomponent materials to conclude definitively that there are often many different multicomponent materials (i.e. with different compositions) that have the same single-phase or multiple-phase structure (such as, for instance, single-phase fcc or two-phase fcc + bcc).<sup>3,16</sup> This can only happen if those particular single-phase or multiple-phase structures occupy large regions in multicomponent phase space\*. We have not yet, however, studied enough multicomponent materials to be able to map out the full extent of any of the individual multicomponent single-phase or multiple-phase fields in multicomponent phase space. We cannot yet, therefore, determine how many multicomponent materials are high-entropy materials and how many are not, though we can be sure that there are very many of each.

The Cantor alloys are the set of multicomponent materials that have a single-phase face-centred cubic (fcc) solid-solution structure, named after the first such material that was discovered, the original Cantor alloy CrMnFeCoNi;<sup>3,4,16,24</sup> similarly, the Senkov alloys are the set of multicomponent materials that have a single-phase body-centred cubic (bcc) solid-solution structure, named after the first such material that was discovered, the original Senkov alloy VNbMoTaW.<sup>3,16,25-27</sup> Very many different Cantor alloys have been manufactured, probably several hundred different materials with different compositions but all with the same single-phase fcc random or near-random solid-solution structure, and there are many more yet to be made;<sup>3,16,24</sup> similarly, very many different Senkov alloys have also been manufactured, again probably several hundred different materials with different compositions but all with the same single-phase random or near-random (in this case) bcc solid-solution structure, and again there are many more yet to be made.<sup>3,16,26,27</sup> There have also been somewhat fewer, but still a reasonable number of different multicomponent materials manufactured so far with different compositions but all with the same single-phase hexagonal close-packed (hcp) random or near-

\* This does not mean that *all* single-phase or multiple-phase structures occupy large regions in multicomponent space, but we have certainly discovered that many of them do.



random solid-solution structure.<sup>3,16</sup> And similar behaviour has also been found in many compounds, i.e. somewhat fewer have been made so far, but there are still very many different multicomponent materials with different compositions but the same compound structure.<sup>3,16</sup> This includes intermetallic compounds such as the multicomponent monoaluminides MAI that have a single-phase B2 CsCl-type ordered bcc structure with all the aluminium atoms on one sublattice and a mixture of different metallic atoms distributed randomly on the other sublattice; ionic compounds such as the multicomponent mono-oxides MO that have a single-phase rock-salt ordered simple-cubic structure with all the oxygen atoms on the anion sublattice and a mixture of different metallic cations distributed randomly or near-randomly on the cation sublattice; and covalent compounds such as the multicomponent diborides MB<sub>2</sub> that have a single-phase C32 TiB<sub>2</sub>-type hexagonal structure, with a mixture of different metallic atoms distributed randomly or near-randomly on the lattice, each covalently bonded by two boron atoms.<sup>3,16</sup> Table 2 lists some of the compounds that have been shown to extend over a range of different compositions in multicomponent phase space.

phase	typical compositions
rock salt	(Li <sub>6.5</sub> Ti <sub>0.5</sub> MnNb)(O <sub>1.7</sub> F <sub>0.3</sub> ) (MgCoNiCuZn)O (TiVZrNb)C; (TiZrNbHfTa)C
fluorite	(ZrYHfCe)O <sub>2</sub> ; (ZrYHfCeGd)O <sub>2</sub> (TiZrSnCeHf)O <sub>2</sub> (Mo <sub>0.5</sub> CePrNdSmGd)O <sub>2</sub>
pyrochlore	(SmEuTbDyLu) <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> (LaCeNdSmEu) <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>
perovskite	(TiMnZrSnHf)SrO <sub>3</sub> ; (TiGeZrSnSn)SrO <sub>3</sub> (TiZrHfNbSn)(SrBa)O <sub>3</sub> (YLaNdSmGd)(CrMnFeCoNi)O <sub>3</sub>
spinel	(AlMnFeCoNi) <sub>3</sub> O <sub>4</sub> ; (AlCrMnFeNi) <sub>3</sub> O <sub>4</sub> ; (CrMnFeCoNi) <sub>3</sub> O <sub>4</sub> ; (CrMnFeNiZn) <sub>3</sub> O <sub>4</sub> (CrMnFeCoNi)Fe <sub>2</sub> O <sub>4</sub>
monoborides	(VCrNbMoTa)B; (VCrNbMoW)B (CrMnFeCoMo)B; (CrNiMoTaW)B
boro-carbo-nitrides	(TiZrNbHfTa)(CN); (TiZrNbTaW)(BCN) (TiZrNbHfTa)(BCN); (ZrNbHfTaW)(BCN)
hexaborides	(YNdSmEuYb)B <sub>6</sub> ; (YCeSmErYb)B <sub>6</sub>
disilicides	(TiZrNbMoW)Si <sub>2</sub> ; (TiNbMoTaW)Si <sub>2</sub>

Table 2: Some examples of single-phase multicomponent compounds.





A sufficiently large number of Cantor alloys has been investigated to allow a rough estimate of the extent of the single-phase fcc Cantor alloy phase field from the different compositions that have been found to adopt a single-phase random or near-random fcc solid-solution structure. The maximum solubilities that have been found for individual components in single-phase fcc Cantor alloys<sup>3,16,24</sup> are shown in Table 3 and Figure 2. Similarly, a sufficiently large number of Senkov alloys have been investigated to allow a rough estimate of the extent of the single-phase bcc Senkov alloy phase field from the different compositions that have been found to adopt a single-phase random or near-random bcc solid-solution structure. The maximum solubilities that have been found for individual components in single-phase bcc Senkov alloys<sup>3,16,26,27</sup> are shown in Table 4 and Figure 3. Solubility levels of any particular component vary, of course, with temperature, material composition and manufacturing method. Maximum solubilities such as those shown in Tables 3 and 4 are, therefore, almost certainly underestimates, since only a limited number of temperatures, material compositions and manufacturing methods have been investigated to date. Nevertheless, as can be seen in Tables 3 and 4, the multicomponent single-phase fcc Cantor and bcc Senkov alloy fields are both very large and complex shaped, each containing enormous numbers of different material compositions. It is likely that this is also the case for many other single-phase fields such as hcp, B2 monoaluminides, rock-salt mono-oxides, C32 diborides, and other phases<sup>3,16</sup> such as those listed in Table 2. These single-phase fields are separated in multicomponent phase space by multiple-phase fields,<sup>3,16</sup> and it is almost certain that these also extend over wide ranges of different compositions. There is clearly a major experimental job to be done in mapping out the size and shape of all the different single-phase and multiple-phase fields in multicomponent phase space.

solute max at%	Au	Pd	Pt	Zn	Nb	V	Ti	Mo
	20	20	20	20	20	20	20	10
	Cu	Al	Cr	Mn	Fe	Co	Ni	
	100	8	25	50	50	50	100	

Table 3: Maximum solute contents in multicomponent single-phase fcc Cantor alloys.

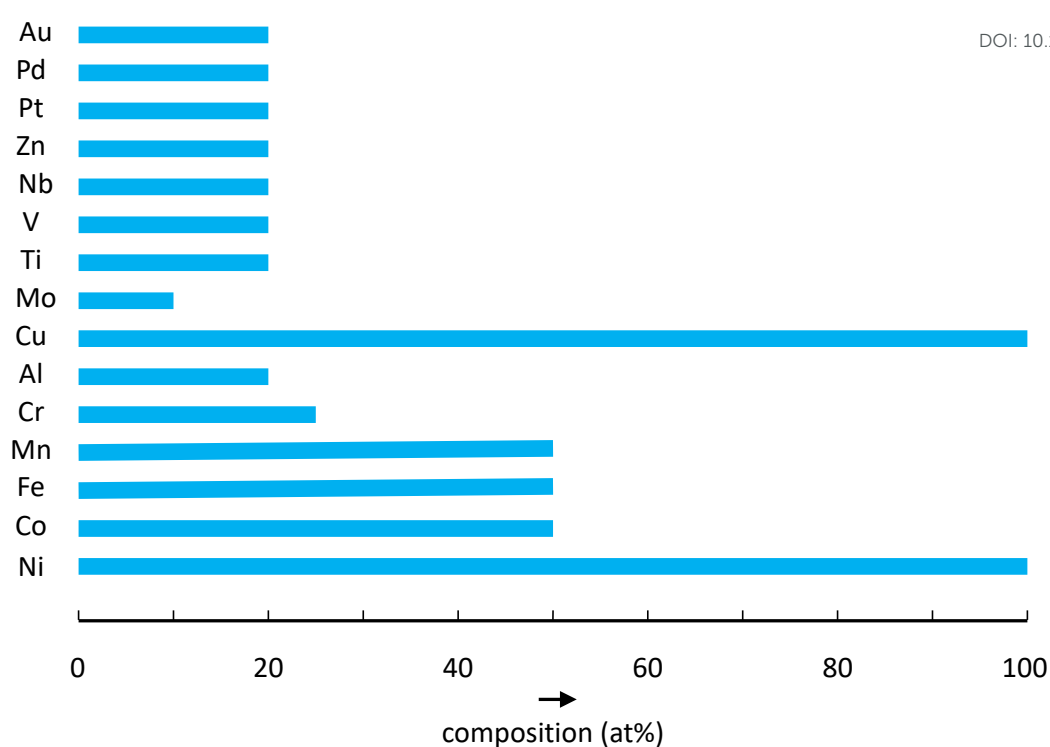
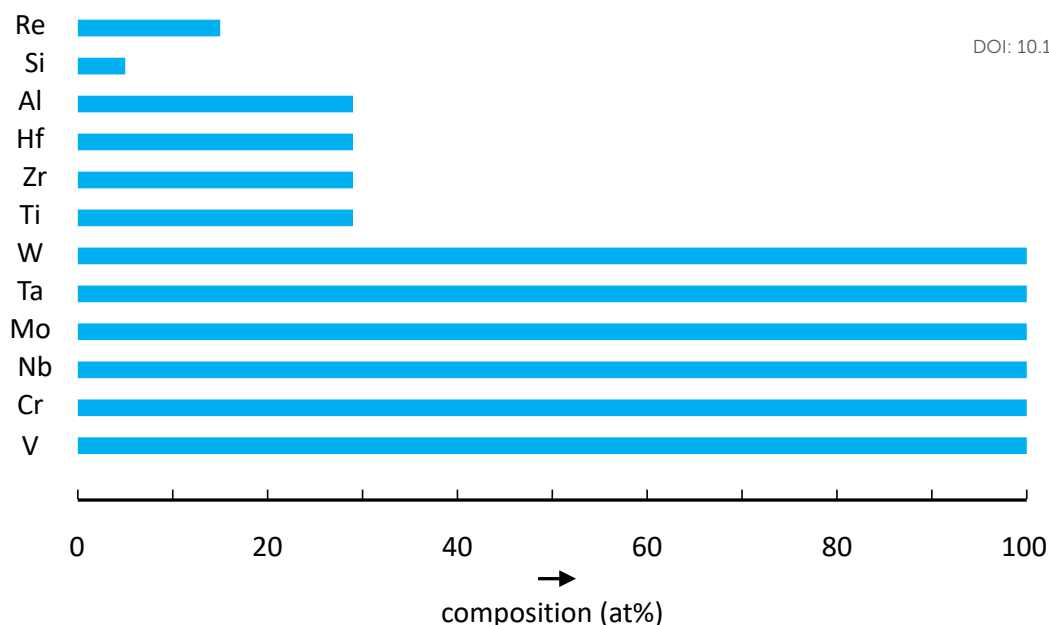


Figure 2: Approximate maximum composition ranges for different components in single-phase fcc Cantor alloys.

solute	Re	Si	Al	Hf	Zr	Ti	W	Ta
max at%	8	2	30	30	30	30	100	100
	Mo	Nb	Cr	V				
	100	100	100	100				

Table 4: Maximum solute contents in multicomponent single-phase bcc Senkov alloys.



View Article Online  
DOI: 10.1039/D5FD00110B

Figure 3: Approximate maximum composition ranges for different components in single-phase bcc Senkov alloys.

## 5. Are multicomponent materials difficult to manufacture?

In the 1970s, 1980s and 1990s, when Jien-Wei Yeh and I were working with colleagues to study the first multicomponent high-entropy materials, it was widely believed that alloying with too much or too many alloying additions was undesirable and a bad idea, which is at least part of the reason why we were not encouraged to undertake our initial studies. It's not entirely clear why this was such a strong and widespread belief, though we can understand in general terms why it had developed. Historically, alloying was invented to improve the properties of particular materials. Thus, tin is added to copper in bronze to make it strong as well as formable;<sup>28</sup> carbon is added to iron in steels for a similar reason;<sup>29</sup> soda (sodium oxide) is added to silica (silicon oxide) in window glass to lower its melting point and make it easier to manufacture;<sup>30</sup> and phosphorus is added to silicon in semiconductors to increase the number of free electrons and enhance its electrical conductivity.<sup>31</sup> Adding too much of an alloying addition, however, or adding too many alloying elements often makes a material difficult to manufacture, because of the formation of large quantities of brittle chemical compounds. Too much copper stannide  $\text{Cu}_6\text{Sn}_5$ , or cementite  $\text{Fe}_3\text{C}$ , or the formation of mullite  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  or silicon phosphide  $\text{SiP}$  make bronze, steel, glass and silicon semiconductors respectively difficult or impossible to manufacture.<sup>28-31</sup> There are many other examples. It is well known, for instance, that the pick up of iron impurities in aluminium alloys needs to be kept lower than a fraction of a percent to prevent the



embrittling effect of iron aluminide compounds;<sup>32</sup> and sulphur impurities in steels need to be kept to similarly low levels to prevent the embrittling formation of iron sulphides.<sup>29</sup> Essentially a very strong taboo has developed over many years against making materials by using excessive alloying.

When alloying additions are increased beyond fairly low levels, the resulting materials often become, as just explained, relatively difficult to process, because of the formation of larger and larger quantities of brittle compounds. This seems to have led, as also just explained, to a strong and widespread tendency to avoid adding too much or too many alloying additions. We have now, however, studied enough multicomponent materials to know that this effect is not always maintained and indeed can often be reversed when we continue to add increasingly higher numbers and higher concentrations of alloying elements.<sup>3,16</sup> When enough alloying additions are made in sufficiently high concentrations, the tendency to form compounds is often, though not always, suppressed, leading instead to the formation in many cases of single-phase random solid-solution phases.<sup>3,16</sup> To summarise: in a large number of multicomponent materials, compound formation is suppressed, leading to a single-phase random solid-solution phase that is often easy to process; in a large number of other multicomponent materials, however, compound formation is not suppressed, leading to the formation of a mixture of multiple compound phases, that is often not easy to process.

## 6. Why is compound formation often suppressed in multicomponent materials?

In a multicomponent material, the molar *Gibbs free energy* of the material  $G$  at any temperature  $T$  is given by.<sup>33-35</sup>

$$G = \sum_i x_i \mu_i^{ss} = \sum_i x_i \mu_i + \Delta G_{mix} = \sum_i x_i \mu_i + \Delta H_{mix} - T \Delta S_{mix}$$

where  $x_i$  is the molar fraction of the  $i$ 'th component,  $\mu_i$  and  $\mu_i^{ss}$  are, respectively, the *chemical potential* (or *molar free energy*) of the  $i$ 'th component before and after mixing to form the solution, and  $\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$ ,  $\Delta H_{mix}$  and  $\Delta S_{mix}$  are, respectively, the *free energy of mixing*, the *heat (or enthalpy) of mixing* and the *entropy of mixing*. The first term on the right hand side is the free energy of the unmixed components, and the last two terms are the free energy change caused by mixing them to form the final material. The heat of mixing  $\Delta H_{mix}$  depends on the set of pairwise, three-way, four-way etc. interaction energies  $\omega_{ij}$ ,  $\psi_{ijk}$ ,  $\chi_{ijkl}$  etc. (essentially the chemical bonding energies) between the different atoms in the material, i.e.  $\Delta H_{mix} = f(\omega_{ij}, \psi_{ijk}, \chi_{ijkl} \dots)$ . The entropy of mixing  $\Delta S_{mix}$  is the sum of two terms  $\Delta S_{mix} = \Delta S_{mix}^c + \Delta S_{mix}^{xs}$ , where  $\Delta S_{mix}^c$  is the configurational entropy of mixing and  $\Delta S_{mix}^{xs}$  is the



excess entropy of mixing. The configurational entropy of mixing  $\Delta S_{mix}^c$  comes mainly from the random mixing of different atoms in any solid-solution phases in the material, with a maximum value when the material forms a single-phase solid solution of  $\Delta S_{mix}^c = -R \sum_i x_i \ln x_i$  where  $R$  is the gas constant, and a minimum value when the material forms a mixture of pure components and stoichiometric fixed-composition compounds of  $\Delta S_{mix}^c = 0^*$ . The excess entropy of mixing  $\Delta S_{mix}^{xs}$  comes from any other changes in disorder in the material and, like the heat of mixing, also depends on the set of pairwise, three-way, four-way etc. interaction energies between the different atoms in the material, i.e.  $\Delta S_{mix}^{xs} = f'(\omega_{ij}, \psi_{ijk}, \chi_{ijkl} \dots)$ , where  $f$  and  $f'$  are different functions. Overall, the Gibbs free energy is given, therefore, by:<sup>33-35</sup>

$$G = \sum_i x_i \mu_i^{ss} = \sum_i x_i \mu_i + \Delta G_{mix} \\ = \sum_i x_i \mu_i + \Delta H_{mix}(\omega_{ij}, \psi_{ijk}, \chi_{ijkl} \dots) + RT \sum_i x_i \ln x_i - T \Delta S_{mix}^{xs}(\omega_{ij}, \psi_{ijk}, \chi_{ijkl} \dots)$$

The first term on the right hand side is the free energy of the unmixed components and is *independent* of the final structure of the material; the sum of the last three terms add up to the free energy of mixing, all of which are *dependent* on the final structure of the material. When a given set of components are mixed together to form a material, it can adopt a variety of different structures, and the final structure is the one with the lowest free energy  $G$ , which is the same, therefore, as the one with the lowest free energy of mixing  $\Delta G_{mix}$ .<sup>33-35</sup>

The heat of mixing  $\Delta H_{mix}$  usually favours compound formation, since it is determined by the interaction energies and the resulting chemical bonding between the different atoms in the material; on the other hand, the entropy of mixing  $\Delta S_{mix}$  usually favours solid-solution formation, since its configurational component is determined by the disorder of mixing the different atoms closely together in the material. As mentioned in the introduction, most of our conventional materials have almost all been made from one, or sometimes two, main components, with relatively few alloying elements added in relatively dilute amounts. In conventional materials, therefore, the free energy of mixing  $\Delta G_{mix}$  and the overall free energy  $G$  of the various possible material structures are usually dominated by the heat of mixing  $\Delta H_{mix}$ . This means that compounds are formed readily when the interaction energies are positive

\* In this paper, the configurational entropy of mixing  $\Delta S_{mix}^c$  is (for convenience, though somewhat unconventionally) taken to be determined by (only) the configurational entropy of mixing different atoms in solid-solution phases in the material; and other contributions to the configurational entropy of mixing, such as the entropy of distributing defects throughout the material (again for convenience, though somewhat unconventionally) are absorbed into the excess entropy of mixing  $\Delta S_{mix}^{xs}$  alongside other contributions to the excess entropy of mixing, such as, for instance, changes in disorder arising from changes in the vibrational, electronic or magnetic states of the atoms in the material.



(i.e. attractive so that chemical bonds can form between the different atoms), so that compound formation increases with increasing number and concentration of the alloying elements; and the entropy of mixing  $\Delta S_{mix}$  is relatively small, so that random or near-random solid solutions are only favourable at high temperatures.

View Article Online  
DOI: 10.1039/D5FD00110B

number of components $c$	$\ln(1/c)$	ideal entropy of mixing $\Delta S_{mix}$ (J/K/mol)	ideal free energy of mixing $\Delta G_{mix}$ at 1,000K (kJ/mol)
2	-0.69	5.76	-5.76
3	-1.10	9.13	-9.13
4	-1.39	11.53	-11.53
5	-1.61	13.38	-13.38
6	-1.79	14.90	-14.90
7	-1.95	16.18	-16.18
8	-2.08	17.29	-17.29
9	-2.20	18.29	-18.29
10	-2.30	19.12	-19.12
20	-3.00	24.91	-24.91
30	-3.40	28.28	-28.28
40	-3.69	30.67	-30.67
50	-3.91	32.53	-32.53

Table 5: Ideal entropy and Gibbs free energy of mixing  $\Delta S_{mix} = -R \ln(1/c)$  and  $\Delta G_{mix} = RT \ln(1/c)$  versus number of components  $c$  in an equiatomic multicomponent material (taking  $R = 8.3145$  J/K/mol).

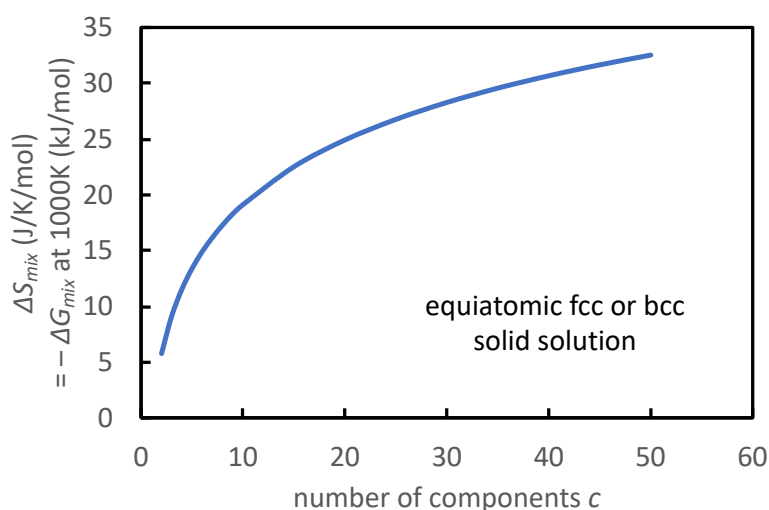


Figure 4: Ideal entropy of mixing  $\Delta S_{mix}$  and ideal free energy of mixing  $\Delta G_{mix}$  at 1,000K for an equiatomic multicomponent material (such as the original Cantor alloy CrMnFeCoNi and Senkov alloy VNbTaMoW) versus the number of components  $c$ .



The situation is different, however, in multicomponent materials, because the entropy of mixing can be much higher.<sup>3,4,11,16</sup> The maximum configurational entropy of mixing in any given alloy system is at the equiatomic composition, i.e.  $\Delta S_{mix}^c = -R \sum_i x_i \ln x_i = -R \ln (1/c)$ , where  $c$  is the number of components, and all  $x_i$  are the same ( $x_i = 0.5$  in a binary alloy, 0.33 in a ternary alloy, 0.25 in a quaternary alloy, etc.). Table 5 shows the resulting maximum ideal\* entropy of mixing  $\Delta S_{mix} = \Delta S_{mix}^c = -R \ln (1/c)$  and the corresponding ideal free energy of mixing  $\Delta G_{mix} = -T\Delta S_{mix}^c = RT \ln (1/c)$  at 1,000 K in such an equiatomic multicomponent material for different numbers of components ranging from  $c = 2$  to 50. The same results are shown graphically in Figure 4. The entropy of mixing in J/K/mol and the free energy of mixing at 1,000 K (1,273°C) in kJ/mol are numerically equal and opposite, the first positive and the second negative. Differentiating:

$$\frac{d\Delta G_{mix}}{dc} = -T \frac{d\Delta S_{mix}^c}{dc} = -\frac{RT}{c} \rightarrow 0 \text{ as } c \rightarrow \infty$$

so the ideal entropy of mixing increases monotonically and the ideal free energy of mixing decreases monotonically with increasing number of components  $c$ , but the rate at which the entropy of mixing increases and the rate at which the free energy of mixing decreases both slow down as the number of components rises.

An entropy of mixing below (approximately) the gas constant  $R$ , i.e.  $\Delta S_{mix} \lesssim 8.3$  J/K/mol or  $c \lesssim 3$ , is lower than most of the interaction energies between the different atoms in a material, and is not, therefore, large enough to suppress compound formation in most materials;<sup>3,16</sup> on the other hand, an entropy of mixing above (approximately) the gas constant  $R$ , i.e.  $\Delta S_{mix} \gtrsim 8.3$  J/K/mol or  $c \gtrsim 3$  is higher than some or all of the interaction energies between the different atoms in a material, and is becoming high enough, therefore, to suppress compound formation in an increasing number of materials as the number of components increases.<sup>3,16</sup> Overall, therefore, compound formation is favoured when there are only low concentrations of a few alloying elements, since the configurational entropy of mixing is too low to outweigh chemical bonding effects; but compound formation becomes increasingly disfavoured when there are high concentrations (e.g. at equiatomic compositions) of many alloying elements (i.e.  $c \gtrsim 3$ ), since the configurational entropy is then becoming high enough to outweigh chemical bonding effects. This explains why multicomponent materials were avoided for many years, when relatively small increases in alloying numbers and concentrations led to excessive compound formation, and the materials were found to be difficult to manufacture. It also

\* In an *ideal* material, there are no chemical interactions between the different atoms in the material, the heat of mixing  $\Delta H_{mix}$  and excess entropy of mixing  $\Delta S_{mix}^{xs}$  are both, therefore, equal to zero, and the ideal free energy of mixing is determined by the configurational entropy of mixing  $\Delta G_{mix} = -RT\Delta S_{mix}^c = RT \ln (1/c)$  for an equiatomic material.



explains our recent and, at first, surprising but now well-established discovery of large single-phase solid-solution regions in multicomponent phase space for equiatomic (and near-equiatomic or, at least, highly concentrated) compositions with five or more components, as discussed in previous sections.

View Article Online

DOI: 10.1039/D5FD00110B

It is worth pointing out, however, that an entropy of mixing even as high as (approximately) three or four times the gas constant  $R$ , i.e.  $\Delta S_{mix} \gtrsim 25 - 35 \text{ J/K/mol}$  or  $c \gtrsim 20$ , is not larger than the interaction energies between the atoms in a material *when they are very different chemically, and the resulting chemical bonds between them are very strong*.<sup>36</sup> It seems likely, therefore, that when the number of components is increased to more than (say) ten or twelve, i.e.  $c \gtrsim 10 - 12$ , the inevitable chemical differences and interaction energies between an increasingly wide range of different elements become too large, and compound formation again takes over. This has not yet been fully established, but it would explain why extensive solid-solution formation has been discovered for multicomponent materials when most of the components are relatively similar chemically, e.g. for single-phase fcc Cantor alloys containing predominantly late transition elements, or single-phase bcc Senkov alloys containing predominantly early transition elements.

## 7. How stable are multicomponent high-entropy materials?

As discussed in previous sections, one of the first major discoveries in multicomponent materials was the single-phase fcc structure of the original Cantor alloy CrMnFeCoNi.<sup>4</sup> This was a big surprise because it was thought that increasing alloying content would lead to excessive compound formation, making multicomponent materials impossible to manufacture. It was particularly surprising for this material, given that only one of the five components (Ni) has an fcc structure at room temperature, and that materials made of binary and ternary mixtures of the five different components are well known to form stable compounds (such as CrMn<sub>3</sub>, CrFe, Cr<sub>3</sub>Co<sub>2</sub>, MnNi, FeNi<sub>3</sub> and FeCo).<sup>4</sup> As also discussed in previous sections, it was further discovered and is now well established that multicomponent single-phase fcc Cantor alloys are formed over a wide range of compositions, including as many as eight or ten or even more mostly late transition-metal components;<sup>3,16,24</sup> that similar behaviour is exhibited by single-phase bcc Senkov alloys, also including as many as eight or ten or even more mostly early transition-metal components;<sup>3,16,26,27</sup> and that similar behaviour is also exhibited in many multicomponent compound structures, including intermetallic, ionic and covalently bonded materials.<sup>3,16</sup> As also discussed in previous sections, we now know that this behaviour is because of the increasing configurational entropy in multicomponent materials with more than three or four components, which can suppress compound formation as long as the multiple components are not too different chemically so that their interaction and chemical-bonding energies are not too large.<sup>3,11,16,36</sup>





Many experimenters have manufactured the original Cantor alloy by many different methods and subjected it to a wide range of different mechanical and thermal treatments, in almost all cases finding it to have a single-phase fcc structure that was easy to manufacture and apparently highly stable.<sup>3,16</sup> There was a certain degree of *schadenfreude*, therefore, when it was first reported that small compound precipitates had been found after extended heat treatment of the original Cantor alloy.<sup>37,38</sup> However, decomposition of the solid solution by precipitation only took place after annealing for several years in a fairly narrow temperature range, and it should not really have been a surprise. It is quite obvious from the functional form of the free energy of a material that entropy effects must become vanishingly small as the temperature decreases (since the second term in  $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$  goes to zero). In fact the third law of thermodynamics says that all materials at absolute zero must form mixtures of perfect single crystals, i.e. mixtures of pure components and fixed-composition compounds. It is similarly quite obvious from the functional form of the free energy of a material that entropy effects must become completely dominant as the temperature increases (since the second term in  $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$  increases without bound). In fact, all materials must become fully mixed atomically at sufficiently high temperatures. All materials will, therefore, in principle separate and decompose from an atomically mixed solution into a mixture of pure components and fixed-composition compounds (sometimes, though not always by precipitation) as they are cooled from high temperature. The only question is how strong are the compound-forming chemical interaction energies between the different atoms in the material relative to the solution-forming configurational entropy of mixing them intimately together; how high, therefore, is the critical temperature above which the equilibrium structure of a material is a solution and below which its equilibrium structure is a mixture of separated phases. In many cases, the chemical interaction energies are strong, much greater than the configurational entropy, and the critical temperature is well above the melting point, so that no solid-solution phase can form but a liquid solution is often formed at high temperatures above the melting point. In many other cases, the chemical interaction energies are less strong, i.e. of a similar size to or somewhat lower than the configurational entropy, and the critical temperature is then below the melting point, so that a solid solution is formed at high temperatures, but it separates into a mixture of pure components and compounds as the material is cooled down to room temperature.<sup>3,16</sup> In some other cases, however, the chemical interaction energies are so much lower than the configurational entropy that the critical temperature is far below the melting point, approaching or even below room temperature, and a solid-solution again forms at high temperatures, but it does not separate into a mixture of pure components and compounds because the critical temperature is too low for significant atomic diffusion to take place.<sup>3,16</sup> To put it another way, solutions are always thermodynamically stable at high temperatures; they sometimes decompose (by precipitation) during cooling to room temperature; but they also sometimes fail





to decompose during cooling to room temperature and are instead kinetically stabilised at low temperatures. Whether decomposition takes place depends on the relative strength of the chemical-bonding interaction energies and the configurational entropy of the solution, with the balance between them determining the critical temperature at which decomposition takes place.

View Article Online

DOI: 10.1039/D5FD00110B

We now know<sup>37,38</sup> that the original Cantor alloy CrMnFeCoNi has a critical temperature approximately equal to 800 °C, so that a single-phase fcc solid solution is thermodynamically stable at high temperatures  $T \gtrsim 800$  °C; precipitation takes place very slowly during annealing for many years in a band of intermediate temperatures  $450$  °C  $\lesssim T \lesssim 750$  °C; and a single-phase fcc solid solution is kinetically stable at low temperatures  $T \lesssim 400$  °C. Similar behaviour is expected for single-phase solid solutions in many different multicomponent materials, i.e. thermodynamic stability at high temperatures, kinetic stability at low temperatures, and (sometimes) decomposition into multiple phases at intermediate temperatures after very extended heat treatment.

## 8. Are high-entropy materials *ideal* solid solutions?

Multicomponent phase space is very large and contains many materials. The answer to many general questions about the materials in multicomponent phase space is, therefore, very often both yes and no. Thus, as discussed previously, many multicomponent materials are found to be high-entropy single-phase solid solutions, but on the other hand, many other multicomponent materials are found not to be high-entropy materials and instead to be multiphase materials. Similarly, many high-entropy materials are ideal or near-ideal (regular\*) random solid solutions with no detectable short-range order, but many other high-entropy materials are found to be non-ideal and non-regular solid solutions, with a noticeable short-range order.<sup>3,16</sup>

In an ideal or regular solid solution, the atoms are distributed at random on the crystal lattice, and the probability of finding an atom of one of the components at any particular lattice point is proportional to its molar fraction, independent of the surrounding environment, i.e. independent of its neighbouring atoms. In a non-regular solid solution, however, the probability of finding an atom of one of the components at any particular lattice point is not proportional to its molar fraction,

---

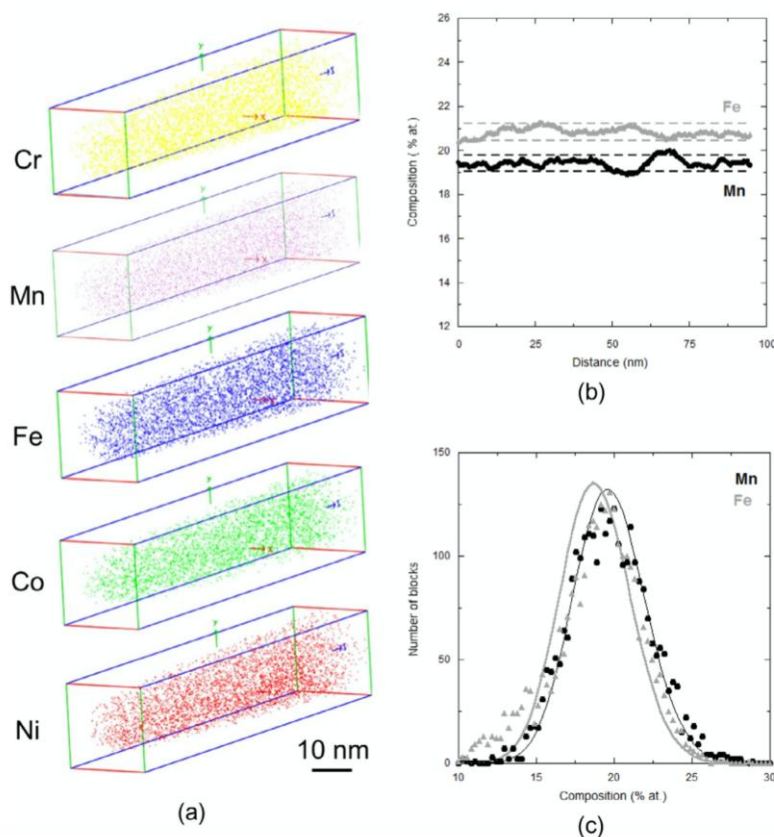
\* An *ideal* solution is one in which the interaction energies between the different atoms in the material are zero, so the heat of mixing is zero and the atoms are completely randomly mixed; a *near-ideal* or *regular* solution is one in which the interaction energies between the different atoms in the material are not zero but are very small, so the heat of mixing is not zero but the atoms are still completely randomly mixed; a *non-regular* solution is one in which the interaction energies between the different atoms in the material are not zero and are not small, so the heat of mixing is not zero, the atoms not completely randomly mixed, and the solution exhibits short-range order ..



and is not independent of its neighbouring atoms. To be more specific, the probability  $p_{ij}^n$  of two atoms of components  $i$  and  $j$  being  $n^{\text{th}}$  near neighbours is given by  $p_{ij}^n = x_i x_j$  in an ideal or regular solid solution, and by  $p_{ij}^n \neq x_i x_j$  in a non-regular solid solution, where  $x_i$  and  $x_j$  are the molar fractions of the  $i^{\text{th}}$  and  $j^{\text{th}}$  components respectively.<sup>39</sup> Non-ideal and non-regular solid solutions exhibit *short-range order*, with an increased probability for either association or disassociation of any particular pair of component atom types  $i$  and  $j$  in any particular near-neighbour shell  $n$ , driven by the non-zero pairwise, three-way, four-way etc. interaction energies between the different atoms  $\omega_{ij}$ ,  $\psi_{ijk}$ ,  $\chi_{ijkl}$  etc. that contribute to the heat of mixing and the corresponding deviation from a random distribution of atoms. Instead of using the probabilities  $p_{ij}^n$  themselves, short-range order effects are usually quantified<sup>39</sup> by the Warren-Cowley short-range order (SRO) parameters  $\alpha_{ij}^n = 1 - (p_{ij}^n/x_i x_j)$ . In an ideal or regular solution, the SRO parameters  $\alpha_{ij}^n$  are all zero; and in a non-regular solution they are either positive or negative for, respectively, the disassociation or association of atoms of components  $i$  and  $j$  as  $n^{\text{th}}$  near neighbours.

Many multicomponent high-entropy materials are *ideal* or *very near-ideal* single-phase solid solutions. The original Cantor alloy is often found to be ideal or very close to ideal, with as far as we can tell a completely random distribution of the five component atoms (Cr, Mn, Fe, Co and Ni) and with no detectable short-range order. This can be seen in the atom probe (AP) measurements in Figure 5, showing an even distribution of each of the five component atoms in CrMnFeCoNi, with statistical analysis confirming a random pattern in each case.<sup>40</sup> Similar results have also been found in other multicomponent materials, such as the single-phase rock-salt-structured mixed Rost oxide (MgCoNiCuZn)O. This can be seen<sup>41</sup> in the high-angle annular dark-field (HAADF) image and associated high-resolution energy-dispersive X-ray (EDX) maps in Figure 6, again showing an even distribution of each of the five cations (Mg, Co, Ni, Cu and Zn) in (MgCoNiCuZn)O. There are also many multicomponent high-entropy materials that are *non-ideal* single-phase solid solutions. The simpler equiatomic three-component single-phase fcc modified Cantor alloy CrCoNi is considerably less homogeneous than the original five-component Cantor alloy, and contains small ~1 nm-sized domains of short-range ordering with enhanced Cr-Co and Cr-Ni and depleted Cr-Cr pairs in the 1<sup>st</sup> near-neighbour shell, i.e. with negative  $\alpha_{\text{CrCo}}^1$  and  $\alpha_{\text{CrNi}}^1$ , and positive  $\alpha_{\text{CrCr}}^1$ , as shown in the high-resolution transmission electron microscope (HRTEM) images<sup>42</sup> in Figure 7. Another example can be seen in the atom-probe (AP) measurements<sup>43</sup> in Figure 8 from a quaternary single-phase bcc modified Senkov alloy ZrNbTaHf, showing short-range clustering of Zr and Hf atoms, i.e. negative  $\alpha_{\text{ZrZr}}^1$ ,  $\alpha_{\text{HfHf}}^1$  and  $\alpha_{\text{ZrHf}}^1$  and corresponding positive  $\alpha_{\text{ZrNb}}^1$ ,  $\alpha_{\text{ZrTa}}^1$ ,  $\alpha_{\text{NbHf}}^1$  and  $\alpha_{\text{TaHf}}^1$  that builds up progressively with annealing time at 1,800 °C (2,073 K), beginning with small nm-sized regions of SRO and finally forming a 3-D phase-separated network on a scale of ~10 nm.





View Article Online  
DOI: 10.1039/D5FD00110B

Figure 5: Atom probe measurements from a recrystallised specimen of the single-phase fcc Cantor alloy CrMnFeCoNi, showing a random atomic-scale distribution of all five components: (a) composition maps (each point is a single atom); (b) composition profiles for Mn and Fe; and (c) random Gaussian composition distributions for Mn and Fe (after Laurent-Brocq et al<sup>40</sup>).

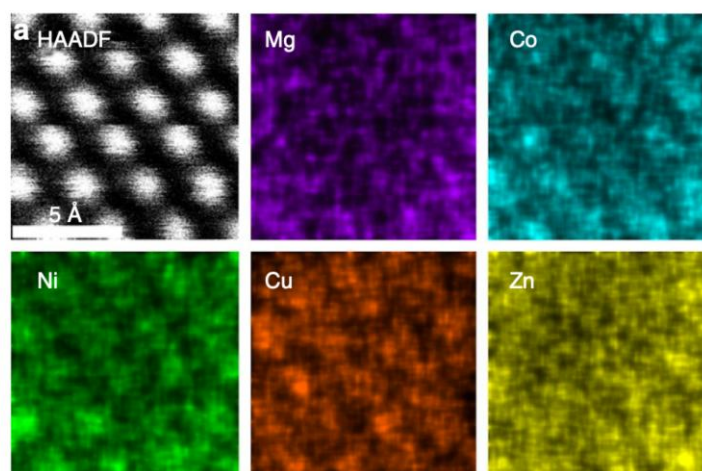


Figure 6: HAADF-STEM atomic image of the single-phase multicomponent oxide (MgCoNiCuZn)O, and corresponding atomic-scale energy-dispersive X-ray (EDX) maps for each of the five cations, showing even intensities from a near-random distribution of cations on the cation sub-lattice (after Rost et al<sup>41</sup>).

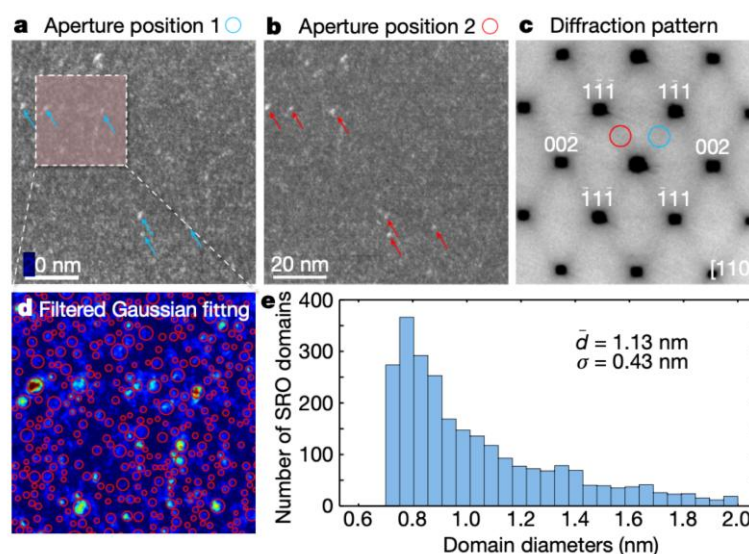


Figure 7: HRTEM of modified Cantor alloy CrCoNi after homogenisation: (a) and (b) filtered dark field images using red and blue selected area diffraction apertures respectively; (c) diffraction pattern; (d) filtered Gaussian fitting showing nm-sized domains; (e) domain size distribution (after Zhang et al<sup>42</sup>).

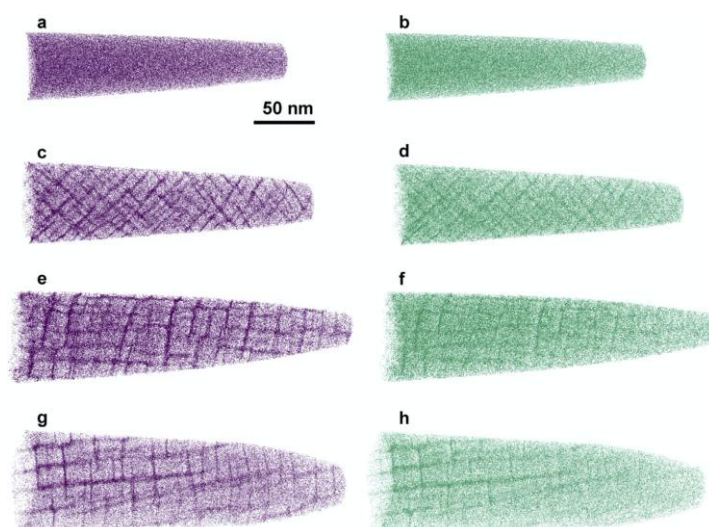


Figure 8: AP composition profiles for Zr (purple) and Hf (green) from modified Senkov alloy ZrNbTaW: (a) and (b) as-cast, and after annealing at 1,800 °C for (c) and (d) 6 hours, (e) and (f) 1 day, and (g) and (h) 4 days (after Maiti and Steurer<sup>43</sup>).



As mentioned in the last section, all high-entropy solid solutions must in principle decompose to form a multiphase structure on cooling to room temperature driven by the interaction energies between the different atoms in the material. But many will not do so, when the interaction energies are relatively weak and the configurational entropy is relatively high, so that the critical temperature for decomposition is too low for significant atomic diffusion to take place.<sup>3,16,36</sup> All high-entropy solid solutions must also in principle exhibit short-range ordering, typically at temperatures in the vicinity of the critical temperature for decomposition (with stable short-range order forming just above the critical temperature, and transitory short-range order forming as a precursor to precipitation just below the critical temperature), again driven by the interaction energies between the different atoms in the material.<sup>3,16,36</sup> But similarly many will not do so, again when the critical temperature is too low for significant atomic diffusion to take place.<sup>3,16,36</sup> Some multicomponent materials, like the original five-component Cantor alloy CrMnFeCoNi, have a low critical decomposition temperature and are, therefore, stable as a high-entropy near-ideal random solid solution, rarely exhibiting short-range order and decomposing only with difficulty after very prolonged heat treatment.<sup>37,38,40</sup> Other multicomponent materials, however, like the three-component modified Cantor alloy CrCoNi or the four-component modified Senkov alloy ZrNbTaHf, have a high critical decomposition temperature and are, therefore, relatively unstable, frequently exhibiting significant short-range order and decomposing easily and rapidly during cooling to room temperature or after relatively short subsequent heat treatment.<sup>42,43</sup>

## 9. What is the local atomic structure in high-entropy materials?

It is rather obvious that multicomponent single-phase materials such as, for instance, the original five-component fcc Cantor alloy CrMnFeCoNi or the original five-component bcc Senkov alloy VNbMoTaW are different from corresponding single-component single-phase materials such as, for instance, pure fcc Cu or pure bcc Fe, because there are different atoms with different properties distributed in a random or near-random way across the different lattice points rather than the same atom with identical properties at every lattice point. But the variation in local structure and properties in multicomponent high-entropy single-phase solid-solution materials is much more extensive and complex, because the structure and properties at any lattice point depend not only on which atom is located there, but also on its interactions with its neighbouring atoms at nearby lattice points.<sup>3,44</sup> In other words, the variation in properties from lattice point to lattice point depends on the range of local atomic environments, i.e. on the range of different local atomic clusters of each atom and its surrounding near-neighbours.



Consider a general lattice with a single atom at each lattice point, and with  $n_1$ ,  $n_2$  and  $n_3$  first, second and third near neighbours respectively. The cluster size of each atom together with its first near neighbours is  $n_1 + 1$  atoms, increasing to  $n_2 + n_1 + 1$  atoms and then to  $n_3 + n_2 + n_1 + 1$  atoms including second and then third as well as first near neighbours. The number of different clusters  $N_1$  of  $n_1 + 1$  atoms,  $N_2$  of  $n_2 + n_1 + 1$  atoms, and  $N_3$  of  $n_3 + n_2 + n_1 + 1$  atoms in a multicomponent equiatomic single-phase material with a random (ideal or regular) arrangement of  $c$  components is given<sup>22</sup> by the *law of permutations with repetition*\*:

$$\begin{aligned} N_1 &= c^{n_1+1} \\ N_2 &= c^{n_2+n_1+1} \\ N_3 &= c^{n_3+n_2+n_1+1} \end{aligned}$$

These are *orientation-dependent* cluster numbers (i.e. equivalent clusters with a different orientation are regarded as different), as is appropriate when we are dealing with properties that depend on orientation, such as dislocation slip, diffusion or magnetisation, when the material is responding to an oriented vector of applied stress, concentration gradient or magnetic field respectively. If cluster orientation is not significant, however, the number of different clusters is smaller because of the number of self-similarity operations  $s$  associated with the crystal symmetry:<sup>45,46</sup>

$$\begin{aligned} N_1 &= (c^{n_1+1})/s \\ N_2 &= (c^{n_2+n_1+1})/s \\ N_3 &= (c^{n_3+n_2+n_1+1})/s \end{aligned}$$

with  $s = 24$  for instance for a cubic crystal<sup>45,46</sup>. These are *orientation-independent* cluster numbers (i.e. equivalent clusters with a different orientation are regarded as the same), as is appropriate when we are dealing with properties that are independent of orientation, such as density or bulk modulus.

Table 6 shows the numbers of oriented and non-oriented local atomic clusters  $N_1$ ,  $N_2$  and  $N_3$  for multicomponent equiatomic single-phase fcc Cantor alloys with  $c$  components, taking for fcc  $n_1 = 12$ ,  $n_2 = 6$  and  $n_3 = 24$ , so the cluster sizes are 13, 19 and 43 atoms respectively.<sup>3,44</sup> Table 7 shows equivalent numbers for

\* We want to calculate how many ways we can pick  $n_1 + 1$  (or, including second or second and third near neighbours,  $n_2 + n_1 + 1$  or  $n_3 + n_2 + n_1 + 1$ ) atoms from a total of  $c$  components. Let the atomic sites in the cluster be labelled 1, 2, 3, etc. up to  $n_1 + 1$  (or  $n_2 + n_1 + 1$  or  $n_3 + n_2 + n_1 + 1$ ). Different *sets* of the  $c$  components distributed across the different atomic sites are clearly different, but different *arrangements* of any given set of  $c$  components across the different atomic sites are also different. In other words we need an *ordered permutation* rather than a *non-ordered combination*. And we need a *permutation with repetition* since each of the different component atoms can be picked more than once<sup>22</sup>.





multicomponent equiatomic single-phase bcc Senkov alloys, taking for bcc  $n_1 = 8$ ,  $n_2 = 6$  and  $n_3 = 12$ , so the cluster sizes are 9, 15 and 27 atoms respectively. The same results are shown graphically in Figures 9 and 10 for fcc and bcc respectively. It is obvious from Tables 6 and 7 and Figures 9 and 10 that the numbers of different local atomic clusters in multicomponent single-phase materials are very large indeed. Many but not all of the properties of a material are determined by interactions between first and second near-neighbour atoms, and many but not all are orientation-dependent, so we concentrate here on the number of oriented, first and second near-neighbour, local atomic clusters, which is just under twenty trillion ( $1.9 \times 10^{13}$ ) for the original single-phase fcc Cantor alloy CrMnFeCoNi and just over thirty billion ( $3.1 \times 10^{10}$ ) for the original single-phase bcc Senkov alloy, both with five components. With six components, the number of oriented, first and second near-neighbour, local atomic clusters increases to just over six hundred trillion ( $6.1 \times 10^{14}$ ) for fcc Cantor alloys and almost half a trillion ( $4.7 \times 10^{11}$ ) for bcc Senkov alloys; and with eight components, it is well over a quadrillion ( $1.4 \times 10^{17}$ ) for fcc Cantor alloys and over thirty trillion ( $3.5 \times 10^{13}$ ) for bcc Senkov alloys. The number of local atomic clusters is, of course, very much larger again if we include third near neighbours and/or increase the number of components to (say) ten or more, as shown in Tables 6 and 7 and Figures 9 and 10. The number in all cases will be somewhat reduced, of course, if there is significant short-range ordering.

number of components $c$	oriented clusters			non-oriented clusters		
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
3	$1.6 \times 10^6$	$1.2 \times 10^9$	$3.3 \times 10^{20}$	$6.4 \times 10^4$	$4.8 \times 10^7$	$1.3 \times 10^{19}$
4	$6.7 \times 10^7$	$2.7 \times 10^{11}$	$7.7 \times 10^{25}$	$2.7 \times 10^6$	$1.1 \times 10^{10}$	$3.1 \times 10^{24}$
5	$1.2 \times 10^9$	$1.9 \times 10^{13}$	$1.1 \times 10^{30}$	$4.8 \times 10^7$	$7.6 \times 10^{11}$	$4.4 \times 10^{28}$
6	$1.3 \times 10^{10}$	$6.1 \times 10^{14}$	$2.9 \times 10^{33}$	$5.2 \times 10^8$	$2.4 \times 10^{13}$	$1.2 \times 10^{32}$
8	$5.5 \times 10^{11}$	$1.4 \times 10^{17}$	$6.8 \times 10^{38}$	$2.2 \times 10^{10}$	$6.0 \times 10^{15}$	$2.7 \times 10^{37}$
10	$10^{13}$	$10^{19}$	$10^{43}$	$4.0 \times 10^{11}$	$4.0 \times 10^{17}$	$4.0 \times 10^{41}$
20	$8.2 \times 10^{16}$	$5.2 \times 10^{24}$	$8.8 \times 10^{55}$	$3.3 \times 10^{15}$	$2.1 \times 10^{23}$	$3.5 \times 10^{54}$
50	$1.2 \times 10^{22}$	$1.9 \times 10^{32}$	$1.1 \times 10^{73}$	$4.8 \times 10^{20}$	$7.6 \times 10^{30}$	$4.4 \times 10^{71}$

Table 6: Number of different oriented and non-oriented local atomic clusters  $N_1$ ,  $N_2$  and  $N_3$  out to first, second and third near neighbours respectively for a multicomponent single-phase fcc material with  $c$  components.





number of components $c$	oriented clusters			non-oriented clusters		
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
3	$2.0 \times 10^4$	$1.4 \times 10^7$	$7.6 \times 10^{12}$	$8.0 \times 10^2$	$5.6 \times 10^5$	$3.0 \times 10^{11}$
4	$2.6 \times 10^5$	$1.1 \times 10^9$	$1.8 \times 10^{16}$	$1.0 \times 10^4$	$4.4 \times 10^7$	$7.2 \times 10^{14}$
5	$2.0 \times 10^6$	$3.1 \times 10^{10}$	$7.5 \times 10^{18}$	$8.0 \times 10^4$	$1.2 \times 10^9$	$3.0 \times 10^{17}$
6	$1.0 \times 10^7$	$4.7 \times 10^{11}$	$1.0 \times 10^{21}$	$4.0 \times 10^5$	$1.9 \times 10^{10}$	$4.0 \times 10^{19}$
8	$1.3 \times 10^8$	$3.5 \times 10^{13}$	$2.4 \times 10^{24}$	$5.2 \times 10^6$	$1.4 \times 10^{12}$	$9.6 \times 10^{22}$
10	$10^9$	$10^{15}$	$10^{27}$	$4.2 \times 10^7$	$4.2 \times 10^{13}$	$4.2 \times 10^{25}$
20	$5.1 \times 10^{11}$	$3.3 \times 10^{19}$	$1.3 \times 10^{35}$	$2.0 \times 10^{10}$	$1.3 \times 10^{18}$	$5.2 \times 10^{33}$
50	$2.0 \times 10^{15}$	$3.1 \times 10^{25}$	$7.5 \times 10^{45}$	$8.0 \times 10^{13}$	$1.2 \times 10^{24}$	$3.0 \times 10^{44}$

Table 7: Number of different oriented and non-oriented local atomic clusters  $N_1$ ,  $N_2$  and  $N_3$  out to first, second and third near neighbours respectively for a multicomponent single-phase bcc material with  $c$  components.

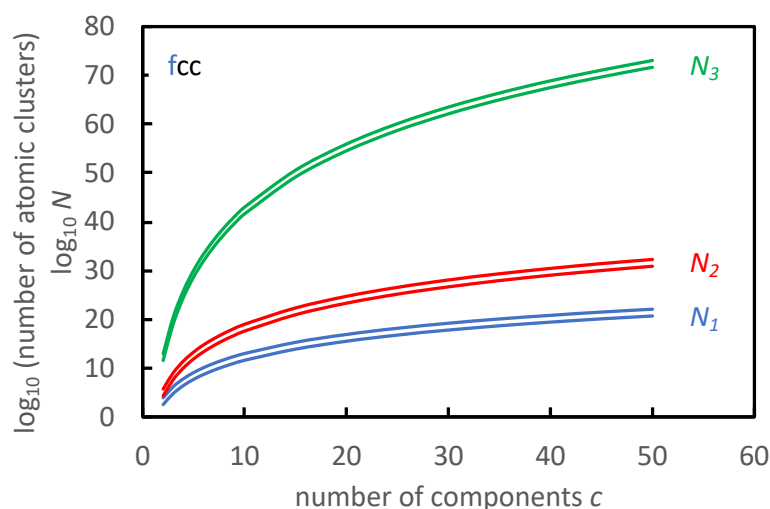
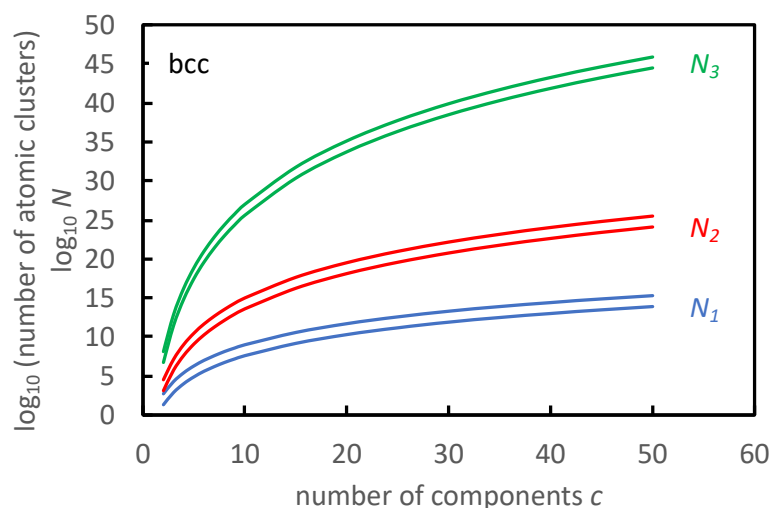


Figure 9: Number of different oriented (upper lines) and non-oriented (lower lines) local atomic clusters out to first ( $N_1$ ), second ( $N_2$ ) and third ( $N_3$ ) near neighbours for a multicomponent single-phase fcc material with  $c$  components.



View Article Online  
DOI: 10.1039/D5FD00110B

Figure 10: Number of different oriented (upper lines) and non-oriented (lower lines) local atomic clusters out to first ( $N_1$ ), second ( $N_2$ ) and third ( $N_3$ ) near neighbours for a multicomponent single-phase bcc material with  $c$  components.

The number of local atomic clusters is very large indeed, and this has an important effect on the spatial consistency of the properties of multicomponent high-entropy single-phase solid solutions such as the fcc Cantor and bcc Senkov alloys.<sup>3,44</sup> Taking the cube root of the number of local atomic clusters gives the size of a piece of the material sufficiently large to include all possible local atomic configurations, i.e. a piece of the material big enough to average reasonably over all the different local atomic environments and, therefore, big enough to represent fully the material and its properties. The linear dimension of such a piece of material is  $\sqrt[3]{1.9 \times 10^{13}} = 2.7 \times 10^4$  clusters or  $\sim 8 \mu\text{m}$  for oriented, first and second near-neighbour clusters in the original single-phase fcc Cantor alloy, and  $\sqrt[3]{3.1 \times 10^{10}} = 3.1 \times 10^3$  clusters or  $\sim 1 \mu\text{m}$  in the original single-phase bcc Senkov alloy, in both cases taking the atomic separation and, therefore, the cluster size as  $\sim 0.3 \text{ nm}$ . In other words, the properties of the original fcc Cantor and bcc Senkov alloys vary from grain to grain if their polycrystalline grain size is below  $\sim 8 \mu\text{m}$  or  $\sim 1 \mu\text{m}$  respectively. To put it another way, the grain size needs to be above  $\sim 8 \mu\text{m}$  or  $\sim 1 \mu\text{m}$  respectively to have a material with consistent properties. And for equiatomic ten-component single-phase fcc Cantor or bcc Senkov alloys, the grain size needs to be above  $\sqrt[3]{10^{19}} = 2.2 \times 10^6$  clusters  $\approx 0.7 \text{ mm}$  or  $\sqrt[3]{10^{15}} = 10^5$  clusters  $\approx 30 \mu\text{m}$  respectively.

This is clearly a very different situation from that which is found in conventional materials consisting of either a single component or a single main component with one or more dilute alloying additions. The extremely large number of different local atomic environments and atomic clusters in multicomponent single-phase fcc and bcc solid solutions such as the Cantor and Senkov alloys (and in other crystal structures such as multicomponent intermetallic and ceramic compounds) plays, therefore, an important role in material properties that depend strongly on local atomic interactions, such as vacancy migration and diffusion, or dislocation slip and

plastic flow.<sup>3,44</sup> The extremely large number of different local atomic environments and atomic clusters in these materials also makes it extremely difficult, in fact almost impossible, to determine their structure and properties with any degree of confidence by fundamental techniques such as *ab initio* molecular dynamics or quantum mechanical modelling that are limited to no more than a thousand or two atoms at best.

View Article Online  
DOI: 10.1039/D5FD00110B

## 10. What is the local atomic strain in high-entropy materials?

component	Goldschmidt atomic radius $r$ (pm)
Cr	128
Mn	127
Fe	126
Co	125
Ni	125
Al	143
Cu	128

Table 8: Goldschmidt atomic radii  $r$  for some of the components used to manufacture fcc Cantor alloys<sup>47</sup>.

Table 8 shows 12-coordinated metallic Goldschmidt atomic radii  $r$  for some of the components that have been used to manufacture multicomponent single-phase fcc Cantor alloys<sup>47</sup>. The maximum difference in atomic size amongst the five different components in the original Cantor alloy CrMnFeCoNi is  $\Delta r = r_{\text{Cr}} - r_{\text{Ni}} = 3$  pm, the corresponding maximum atomic misfit is  $\delta_{\text{max}} = (r_{\text{Cr}} - r_{\text{Ni}})/r_{\text{Ni}} = 2.4\%$ , and the root-mean-square (RMS) average atomic misfit is  $\delta_{\text{av}} = \sqrt{\sum_i x_i \{(r_i - r_{\text{av}})/r_{\text{av}}\}^2} = 0.9\%$ , where summation is over all the components  $i = 1$  to  $n$ ,  $x_i = 0.2$  is the mole fraction of the  $i$ 'th component, and  $n = 5$  is the number of components. The values of  $\Delta r$ ,  $\delta_{\text{max}}$  and  $\delta_{\text{av}}$  remain unchanged when Cu is included in a modified CrMnFeCoNiCu<sub>x</sub> Cantor alloy; but they are somewhat larger when Al instead of Cu is included in a modified Al<sub>x</sub>CrMnFeCoNi Cantor alloy:  $\Delta r = 18$  pm,  $\delta_{\text{max}} = 14.4\%$ , and  $\delta_{\text{av}} = 1.4\%$ , for the maximum Al solubility with  $x_{\text{Al}} = 8\%$  and  $x_{i \neq \text{Al}} = 18.4\%$ . We might expect, therefore, to find lattice distortions on a scale of somewhat under  $\sim 1$  pm or 1% on average, rising to a maximum of  $\sim 3$  pm or  $\sim 3\%$  in the original Cantor alloy, and a bit higher in some of the modified Cantor alloys such as those containing Al. These calculations are rather approximate since they ignore effects such as short-range order, non-ideality, relaxation, and electronic distortions. More detailed analyses have used measured lattice parameters, different definitions of atomic misfit and lattice distortion, and *ab initio* calculations, but all lead to similar predicted local lattice distortions<sup>48-51</sup> of  $\Delta r \approx 3.3$ – $6.6$  pm.



Lattice distortions have been measured in multicomponent solid solutions by synchrotron X-ray diffraction (XRD)<sup>48</sup>, neutron diffraction (ND)<sup>52</sup> and extended X-ray absorption fine-structure analysis (EXAFS)<sup>49,53</sup>. The measurements are difficult because of the need to separate static displacements caused by lattice distortions, dynamic displacements caused by thermal vibrations, and bulk lattice strain. Sophisticated fitting software is used with high-quality diffraction data to separate out different effects within the measured broadening of diffraction peaks. Okamoto et al<sup>48</sup> used single-crystal synchrotron X-ray diffractometry to measure atomic displacements in the original Cantor alloy of  $4.8$  and  $7.7 \pm 0.5$  pm at  $25$  K and  $300$  K respectively, indicating a static displacement (at  $25$  K) of  $\Delta r \approx 4.8$  pm and a thermal displacement (at  $300$  K) of  $7.7 - 4.8 = 2.9$  pm. Owen et al<sup>52</sup> used neutron powder diffractometry to measure partial distribution functions in the original Cantor alloy, with different peak widths between the Cantor alloy and pure Ni corresponding to static distortions of  $\Delta r \approx 2 \pm 0.5$  pm and the underlying peak width giving thermal distortions of  $\sim 18 \pm 0.5$  pm. Oh et al<sup>49</sup> used EXAFS spectra from the original Cantor alloy to obtain mean elemental distortions of  $+0.1\%$ ,  $+0.5\%$ ,  $-0.1\%$ ,  $-0.4\%$  and  $-0.1\%$  for Cr, Mn, Fe, Co and Ni respectively\*, correlating roughly with the Goldschmidt atomic radii in Table 8, and with maximum distortions up to  $\sim 3\%$  of  $r_{av}$  ( $= 126.2$  pm), i.e.  $\Delta r \approx 3.8$  pm.

Table 9 shows experimental and calculated results for local distortions  $\Delta r$  in the original fcc Cantor alloy CrMnFeCoNi. In conclusion, there are small but significant local lattice distortions that fluctuate randomly over large distances (because of the enormous number of different local atomic cluster configurations), with an average value of just under  $1$  pm (corresponding to just under  $\sim 1\%$  strain), reaching a maximum value of  $\sim 2$ – $6$  pm (corresponding to  $\sim 2$ – $6\%$  strain). Similar measurements and calculations indicate, as expected, somewhat smaller lattice distortions in simpler fcc Cantor alloy compositions such as CrFeCoNi<sup>50,53-55</sup>, but somewhat larger lattice distortions in modified Cantor alloy compositions containing additional components such as VFeCoNi<sup>56</sup> and FeNiCoCrPd<sup>55</sup>.

	method	maximum local atomic distortion $\Delta r$ (pm)
calculations	Goldschmidt radii	3.0
	<i>ab initio</i>	3.3–6.6
experiments	synchrotron XRD	4.8
	neutron diffraction	2.0
	EXAFS	3.8

\* Positive and negative values represent increased and decreased bond lengths respectively, corresponding to local atomic expansion and compression strains respectively



Table 9: Experimental and calculated values for the maximum local atomic distortion  $\Delta r$  in the equiatomic fcc Cantor alloy CrMnFeCoNi, obtained by a variety of different methods<sup>47-52</sup>.

View Article Online  
DOI: 10.1039/D5FD00110B

component	Goldschmidt atomic radius $r$ (pm)
V	135
Nb	145
Mo	145
Ta	145
W	135
Al	143
Ti	140
Zr	155
Hf	155

Table 10: Goldschmidt atomic radii  $r$  for components used to manufacture bcc Senkov alloys<sup>47</sup>.

Table 10 shows 12-coordinated metallic Goldschmidt atomic radii  $r$  for some of the components that have been used to manufacture multicomponent single-phase bcc Senkov alloys<sup>47</sup>. The maximum difference in atomic size amongst the five different components in the original Senkov alloy VNbMoTaW is  $\Delta r = r_{\text{Nb}} - r_{\text{V}} = 10$  pm, the corresponding maximum atomic misfit is  $\delta_{\text{max}} = (r_{\text{Nb}} - r_{\text{V}})/r_{\text{V}} = 7.4\%$ , and the root-mean-square (RMS) average atomic misfit is  $\delta_{\text{av}} = \sqrt{\sum_i x_i \{(r_i - r_{\text{av}})/r_{\text{av}}\}^2} = 3.5\%$ . The values of  $\Delta r$ ,  $\delta_{\text{max}}$  and  $\delta_{\text{av}}$  remain unchanged when either Al or Ti are included in modified  $\text{Al}_x\text{VNbMoTaW}$  or  $\text{Ti}_x\text{VNbMoTaW}$  Senkov alloys respectively; but they are somewhat larger again when either Zr or Hf are included in modified  $\text{VNbZr}_x\text{MoTaW}$  or  $\text{VNbMoHf}_x\text{TaW}$  Senkov alloys respectively, for an equiatomic six-component alloy with  $x_i = 16.67\%$ . We might expect, therefore, to find lattice distortions on a scale of  $\sim 4$  pm or  $\sim 4\%$  on average rising to a maximum of  $\sim 7$ – $10$  pm or  $\sim 10\%$  in the original Senkov alloy, and still higher in some of the modified Senkov alloys such as those containing Zr or Hf. These calculations are again rather approximate since they ignore effects such as short-range order, non-ideality, relaxation, and electronic distortions. Other analyses of the lattice distortion have again used *ab initio* calculations, leading to similar predicted local lattice distortions of  $\Delta r \approx 5$ – $15$  pm<sup>50</sup>.





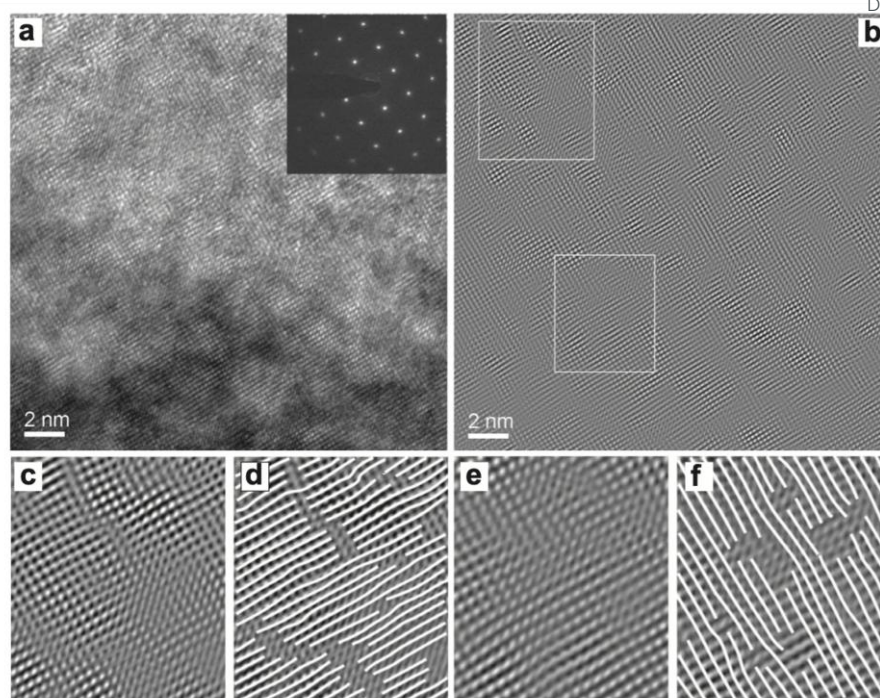


Figure 11: HRTEM images of the equiatomic quaternary NbMoTaW bcc Senkov alloy: (a) bright-field (BF) image with [100] zone axis; (b) corresponding inverse fast-Fourier transform; (c) and (e) enlarged images of the boxes in (b); and (d) and (f) traces corresponding to (c) and (e) to show the lattice distortions (after Zou et al<sup>57</sup>).

Zou et al<sup>57</sup> used single-crystal X-ray diffractometry to measure average atomic displacements in the original Senkov alloy, indicating static and dynamic lattice distortions of  $\Delta r \approx 7.4$  and  $6.1 \pm 0.5$  pm respectively. Lattice distortions on a scale of tens of pm have also been observed by Zou et al<sup>57</sup> in the same alloy by high-resolution transmission electron microscopy (HRTEM), with [100] zone axis images containing distorted {110} planes, as shown in Figure 11. Guo et al<sup>58</sup> used a combination of synchrotron X-ray diffractometry (XRD) and time-of-flight (TOF) neutron diffractometry to obtain radial distribution functions from a modified ternary Senkov alloy ZrNbHf, with an overlap of the first and second near-neighbour peaks corresponding to lattice distortions of  $\sim 9.5$  pm, and similar combined XRD and ND results on a quaternary modified Senkov alloy ZrNbTaHf showed static and dynamic thermal distortions of 13.7 and 2.4 pm respectively<sup>59</sup>.

Table 11 shows experimental and calculated results for maximum local distortions  $\Delta r$  in bcc Senkov alloys. In conclusion, there are again significant local lattice distortions in the bcc Senkov alloys, somewhat larger than those found in the fcc Cantor alloys, that again fluctuate randomly over large distances (because of the enormous number of different local atomic cluster configurations), with average

values of ~4 pm (corresponding to ~4% strain), reaching maximum values of ~5–20 pm (corresponding to >5% strain).

View Article Online  
DOI: 10.1039/D5FD00110B

	method	alloy	maximum local atomic distortion $\Delta r$ (pm)
calculations	Goldschmidt radii	VNbMoTaW	10.0
		AlVNbMoTaW	
		TiVNbMoTaW	
	Goldschmidt radii	VNbZrMoTaW	20.0
		VNbMoHfTaW	
	<i>ab initio</i>	TiVNb	5–15
experiments		AlTiVNb	
		TiZrNbTaHf	
	XRD	NbMoTaW	4.8
	synchrotron XRD & ND	ZrNbHf	9.5
	synchrotron XRD & ND	ZrNbTaHf	13.7

Table 11: Experimental and calculated values for the maximum local atomic distortion  $\Delta r$  in the bcc Senkov alloys, obtained by a variety of different methods.<sup>47,50,56-59</sup>

It is highly likely that similar substantial local atomic strains are to be found in all multicomponent high-entropy single-phase solid-solutions, extending over large distances, and influencing many of their properties.

## 11. What is the effect of varying local atomic strain?

### 11.1 Vacancies and diffusion

Atomic motion leads to the degradation of crystalline materials when they are exposed, for instance, to high temperatures, irradiation or a corrosive environment. And atomic motion usually takes place in crystalline materials by vacancy migration.<sup>35,60,61</sup> The probability of finding a vacancy at any lattice point  $p_v$  and the probability of vacancy motion (i.e. of an adjacent atom jumping into it)  $p_m$  are both given at any temperature  $T$  by Boltzmann's equation<sup>35,60,61</sup>:

$$p_v \propto \exp \left( -\frac{\Delta E_v}{kT} \right)$$

$$p_m \propto \exp \left( -\frac{\Delta E_m}{kT} \right)$$



where  $\Delta E_v$  and  $\Delta E_m$  are the vacancy formation and migration energies respectively and  $k$  is Boltzmann's constant. In a single component pure material,  $\Delta E_v$  and  $\Delta E_m$  and, therefore,  $p_v$  and  $p_m$  are all independent of position because all the lattice sites are identical. Atomic motion takes place, therefore, via a random walk and obeys Fick's laws, with a diffusion coefficient  $D$  that depends on  $p_v$  and  $p_m$ :

$$D \propto p_v p_m = D_o \exp\left(-\frac{Q}{kT}\right)$$

where  $D_o$  and  $Q = \Delta E_v + \Delta E_m$  are, respectively, the frequency factor and the activation energy for diffusion<sup>35,60,61</sup>.

Atomic motion in a concentrated multicomponent high-entropy solid solution such as an fcc Cantor alloy or a bcc Senkov alloy is more complex because of the wide variety of different local atomic structures and associated lattice distortions surrounding the vacancies, and a correspondingly wide range of different vacancy formation and migration energies  $\Delta E_v$  and  $\Delta E_m$ , depending upon where the vacancy is and what exactly are its surrounding atoms.<sup>3,44</sup> There is an enormous number of different local atomic clusters surrounding each individual type of atom in a multicomponent solid solution (as discussed previously and as shown in Tables 6 and 7 and Figures 9 and 10): and there is a similarly enormous number of different local atomic clusters surrounding the vacancies in a multicomponent solid solution or, to put it in another way, there is an enormous number of different vacancy structures.<sup>3,44</sup>

There is little or no lattice distortion in a single-component pure material, and the variation of energy as an individual vacancy hops from one lattice site to another consists of a series of *identical* jumps, as shown schematically in Figure 12, from identical wells at each of the lattice sites all with the same well energy  $E_w$ , over identical saddle points midway between each of the lattice sites all with the same saddle-point energy  $E_s$ . In a concentrated multicomponent high-entropy solid solution, however, the situation is very different, because of the large number of vacancy structures and associated local lattice distortions at different lattice points, the corresponding range of vacancy formation and migration energies  $\Delta E_v$  and  $\Delta E_m$ , and the corresponding spread of well and saddle-point energies  $E_w$  and  $E_s$ . The variation in energy of an individual vacancy as it hops from one lattice site to another consists instead, therefore, of a series of *variable* jumps, as also shown schematically in Figure 12, from variable wells at the different lattice sites all with different well energies  $E_w$ , over variable saddle points midway between each of the lattice sites all with different saddle-point energies  $E_s$ .



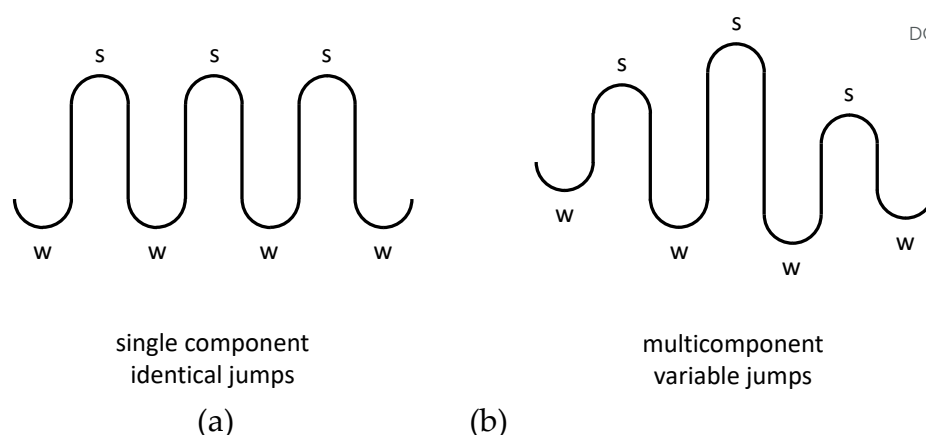


Figure 12: Schematic variation of energy as a vacancy hops from lattice site to lattice site: (a) in a single component material with all jumps identical; and (b) in a multicomponent material with variable jumps (s = saddle point energy; w = energy well).

The overall rate of atomic diffusion and, therefore, the diffusion coefficient in concentrated multicomponent high-entropy solid-solution materials is affected in a variety of ways<sup>44,62</sup> by the variation in vacancy formation and migration energies  $\Delta E_v$  and  $\Delta E_m$ , and the corresponding spread of well and saddle point energies  $E_w$  and  $E_s$ . High-energy barriers in some places make it particularly difficult for a vacancy to hop from one site to the next; low energy barriers in other places make it particularly easy for a vacancy to hop from one site to the next; and a vacancy can be trapped in some places, hopping backwards and forwards between adjacent or near-adjacent lattice points, or going round and round in circles. The overall impact of these different effects is, not surprisingly, quite complex, and strictly speaking diffusion is no longer truly random spatially, since the lattice points are no longer all identical. We have not yet made much experimental or theoretical progress towards developing a detailed understanding of this complex range of different vacancy behaviours and the resulting overall rates of atomic diffusion. Thomas and Patala<sup>62</sup> calculated the expected spread of well and saddle-point energies  $E_w$  and  $E_s$  for vacancies hopping between adjacent lattice sites at 1,000°C in the original five-component single-phase fcc Cantor alloy CrMnFeCoNi, using a nudged elastic band (NEB) molecular dynamics (MD) method with a modified embedded atom method (MEAM) potential within the Sandia Labs LAMMPS software. The diffusion coefficient  $D$  was found to be fairly sensitive to the spread of energy values during the hopping process, varying between a half and five times a reference diffusion coefficient  $D^*$  in an equivalent material with the same barrier energy of 0.81 eV but with constant well and saddle-point energies. The exact results obtained by these calculations should be treated with considerable caution (as with other modelling results), since they average over only about three thousand vacancy hops, well below the total number of almost twenty trillion different vacancy structures

(including first and second near neighbours). Nevertheless, the results show clearly that diffusion is slower when there is a wide spread of well energies (high  $\sigma_w$ ) because vacancies can become trapped in the lowest energy wells; but is faster when there is a wide spread of saddle-point energies (high  $\sigma_s$ ) because vacancies can take migration paths that simply avoid the highest energy barriers.

View Article Online

DOI: 10.1039/D5FD00110B

There has been considerable discussion in the previous literature about whether or not diffusion is slower in multicomponent high-entropy solid-solution single phases relative to pure materials,<sup>63-67</sup> somewhat confused by the difficulties of deciding what are appropriate comparison materials, and the complexity of measuring diffusion coefficients from multicomponent material diffusion couples. There is, however, little doubt that diffusion is quite slow in many but not all cases,<sup>3,63,64</sup> often by up to about a half or one order of magnitude, with correspondingly slow diffusion-controlled processes such as precipitation and recrystallisation,<sup>3,16,24</sup> almost certainly caused by the wide variety of local atomic structures as described above. Clearly we need to develop more detailed theories of diffusion in multicomponent high-entropy solid-solution materials such as the fcc Cantor and bcc Senkov alloys, based on non-Fickian atomic percolation through complex structural landscapes with varying lattice-point and saddle-point energies.

## 11.2 Dislocations and slip

Plastic flow, fracture toughness and formability in crystalline materials is controlled largely by the way in which dislocations move under the action of an applied stress. There is an excess energy per unit length of a dislocation  $\Delta E_d$ , arising partly from the displacement of atoms along the dislocation line itself, i.e. in the dislocation core, and partly from smaller atomic displacements outside the core. The excess energy per unit length or line tension of a dislocation  $\Delta E_d$  is given by:<sup>35,68,69</sup>

$$\Delta E_d = E_c + \frac{\alpha G b^2}{4\pi} \ln \frac{R}{r_c} \approx G b^2$$

where  $E_c$  and  $r_c$  are the energy and radius of the highly distorted dislocation core region,  $G$  is the shear modulus,  $R$  is the dislocation spacing, the factor  $\alpha = 1$  or  $1 - \nu$  for screw or edge dislocations respectively, and  $\nu$  is Poisson's ratio. In most single-component crystalline materials, the dislocation energy is high and dislocations are difficult to create and immobile, so the materials are hard but brittle, with little plasticity, fracture toughness or formability. In single-component close-packed metals, however, the dislocation energy is much lower and dislocations are relatively easy to create and move,<sup>35,68,69</sup> so the materials are much softer but are ductile, tough (fracture resistant) and formable, with dislocation motion preventing the build-up of local high stresses and cracking.<sup>35,68,69</sup> The overall flow stress  $\tau$





required to move a dislocation can usually be treated as a straightforward sum of different contributions to the material strength:<sup>1,2</sup>

View Article Online

DOI: 10.1039/D5FD00110B

$$\tau = \tau_o + \tau_{wh} + \tau_{ss} + \tau_{gb} + \tau_{ph}$$

where  $\tau_o$  is the lattice friction stress, and  $\tau_{wh}$ ,  $\tau_{ss}$ ,  $\tau_{gb}$  and  $\tau_{ph}$  are strengthening contributions from work hardening, solution hardening, grain boundaries and precipitates respectively.

Dislocation motion in a concentrated multicomponent high-entropy solid-solution such as an fcc Cantor alloy or a bcc Senkov alloy is more complex, because of the wide variety of different local atomic structures and associated lattice distortions surrounding atoms along the length of the core of a dislocation<sup>3,44</sup> (as discussed previously and as shown in Tables 6 and 7 and Figures 9 and 10), and a correspondingly wide variation in the dislocation core energy and line tension  $E_c$  and  $\Delta E_d$ . The atomic structure varies widely from point to point along a dislocation line, and also from time to time at any given point on a dislocation line as it moves under the action of an applied stress.<sup>3,44</sup> Once again, we have not yet made much experimental or theoretical progress towards developing a detailed understanding of this complex range of different local dislocation structures, the resulting dislocation motions and interactions, and, therefore, the overall plasticity in multicomponent high-entropy materials.

Dislocations in fcc Cantor alloys are in some ways found to be similar to those observed previously in pure fcc metals and dilute fcc binary alloys with a relatively low stacking fault energy.<sup>70-72</sup> Unlike pure fcc metals and dilute binary fcc alloys, however, the dislocations in multicomponent single-phase fcc Cantor alloys are wavy rather than straight on a near-atomic scale, with a wide variation along the dislocation line in the separation of the two Shockley partials (and, therefore, the width of the stacking fault between them and corresponding stacking fault energy), and a much higher shear stress needed for slip along the {111} planes.<sup>70-76</sup> An example of a wavy dislocation and measurements of the varying partial separation and corresponding stacking fault energy<sup>73</sup> are shown in Figure 13 for the original fcc Cantor alloy CrMnFeCoNi. These effects are all caused by the variation in local atomic structures along the dislocation lines as described above, with the associated local lattice strains acting as pinning centres for the dislocations. Okamoto et al<sup>79</sup> used high-resolution weak-beam imaging to make a large number of measurements of the separation between partials along the length of dislocation lines in the original fcc Cantor alloy CrMnFeCoNi, which were found to be variable in the range  $d = 3\text{--}8$  nm, corresponding to stacking fault energies in the range  $\gamma_{sf} = 25\text{--}35$  mJ/m<sup>2</sup>. Similar wavy dislocations with varying separation of partials along the dislocation line have also been seen in a number of multicomponent single-phase fcc Cantor alloys using a



variety of transmission electron microscope techniques and also by atomistic *ab initio* modelling techniques.<sup>74-79</sup>

View Article Online  
DOI: 10.1039/D5FD00110B

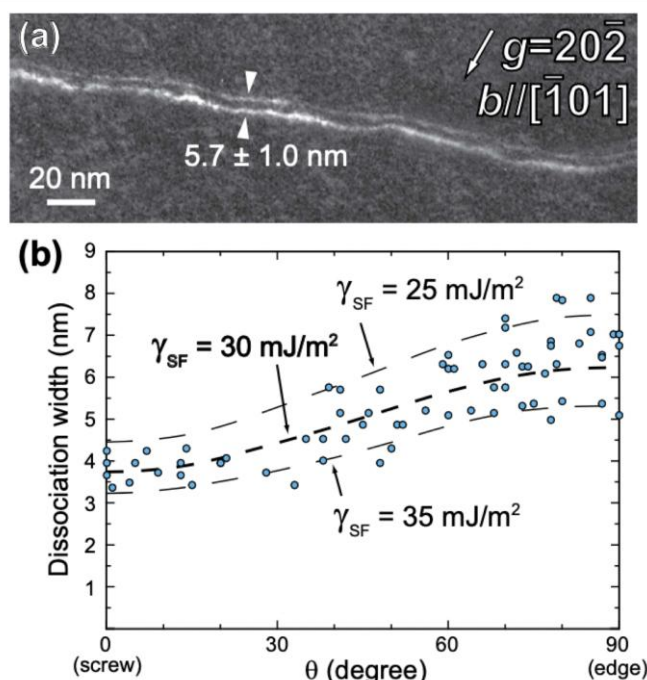


Figure 13: (a) High resolution weak-beam image of a  $\frac{1}{2}\langle 110 \rangle$  dislocation in the original fcc Cantor alloy CrMnFeCoNi showing a wavy dislocation line and separation into two  $\frac{1}{6}\langle 112 \rangle$  Shockley partials; and (b) partial separation distance  $d$  in a large number of dislocations as a function of dislocation orientation  $\theta$ , ranging from pure screw ( $\theta = 0^\circ$ ) to pure edge ( $\theta = 90^\circ$ ) (after Okamoto et al<sup>73</sup>).

Dislocation structures in bcc Senkov alloys are also found to be similar in some ways to those observed previously in pure bcc metals and dilute bcc binary alloys.<sup>80-</sup>  
<sup>83</sup> Unlike pure bcc metals and dilute binary bcc alloys, however, the dislocations in multicomponent single-phase bcc Senkov alloys are, like the fcc Cantor alloys, wavy rather than straight on a near-atomic scale, and require a much higher shear stress for slip along the different planes.<sup>80-83</sup> These effects are again, like the fcc Cantor alloys, caused by the variation in local atomic structures along the dislocation lines, with the associated local lattice strains acting as pinning centres for the dislocations.

There has been some success in explaining the strength of multicomponent high-entropy solid-solution materials such as the fcc Cantor alloys and bcc Senkov alloys, based on averaging the the pinning effects of varying local atomic structures along the dislocation lines.<sup>84-89</sup> Clearly, we still need to investigate experimentally what must be a much wider range of varying dislocation behaviour, and thus develop a more detailed theory of overall dislocation dynamics, as dislocations move about and interact within a complex landscape of varying local atomic structure and associated varying dislocation energies.



As already mentioned, a much higher shear stress is needed for dislocation slip in multicomponent high-entropy solid-solution single-phase materials such as the fcc Cantor alloys and bcc Senkov alloys. This is caused by the variation in local atomic structures along the dislocation lines, with the associated local lattice strains acting as pinning centres for the dislocations.<sup>3,44</sup> Effectively this corresponds to raising the lattice friction stress because of the dense number of pinning centres created by a high concentration of many different types of solute atoms. The shear flow stress can be rewritten as:<sup>3,44</sup>

$$\begin{aligned}\tau &= \tau_o + \tau_{wh} + \tau_{ss} + \tau_{gb} + \tau_{ph} \\ &\approx \tau_o + \tau_{wh} + \tau_{gb} \\ &\approx \tau_o + 2\alpha G b \rho^{1/2} + \beta d^{-1/2}\end{aligned}\quad (25)$$

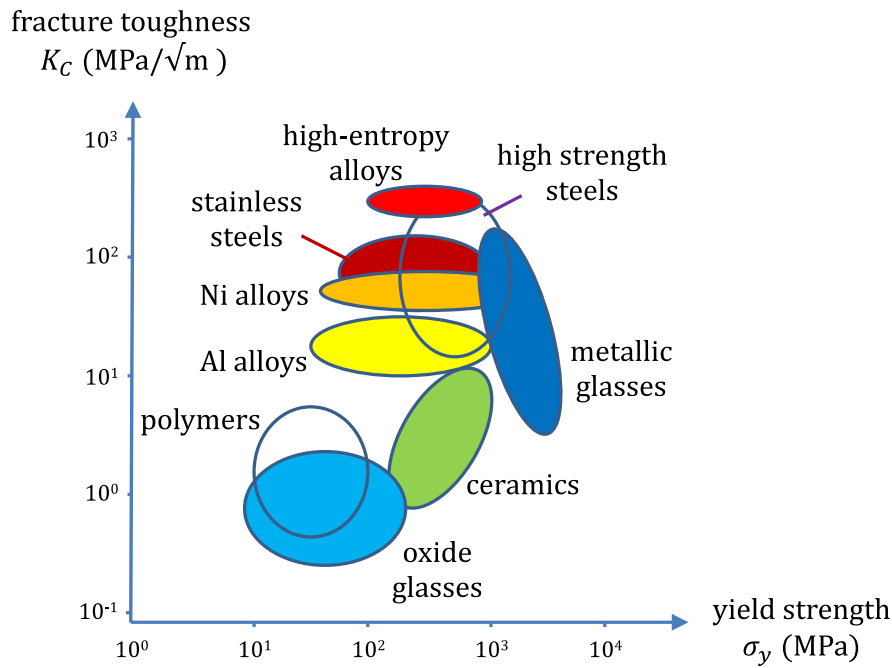


Figure 14: Schematic Ashby map of fracture toughness  $K_c$  versus yield strength  $\sigma_y$  for multicomponent high-entropy alloys compared with high-strength steels, nickel superalloys, hard ceramics, and metallic and oxide glasses (redrawn<sup>14</sup> from Gludowatz et al<sup>90</sup> and Li et al<sup>91</sup>).

where  $\tau_{ph}$  is taken as zero in a material with no precipitates; the solid solution strengthening  $\tau_{ss}$  is incorporated into an enhanced lattice friction stress  $\tau_o$ ; work hardening is given by a Taylor parabolic variation with dislocation density  $\rho$ , i.e.  $\tau_{wh} \approx 2\alpha G b \rho^{1/2}$ , where  $\alpha$  is a constant,  $G$  is the shear modulus, and  $b$  is the Burgers vector; and grain-boundary hardening is given by a Hall-Petch variation with grain



size  $d$ , i.e.  $\tau_{gb} = \beta d^{-1/2}$ , where  $\beta$  is another constant. Overall, this means that multicomponent fcc Cantor alloys and bcc Senkov alloys have outstanding combinations of strength and ductility, as shown in the Ashby map<sup>90</sup> in Figure 14. According to Li et al.<sup>91</sup> “the CrMnFeCoNi alloy represents one of the toughest materials reported to date, with a plane-strain fracture toughness,  $K_{1c}$ , that exceeds 200 MPa $\sqrt{m}$  and with an outstanding tensile strength exceeding 1 GPa”. Much research is now underway to improve even further the mechanical properties of these multicomponent high-entropy materials by additional strengthening mechanisms such as reducing the grain size, work hardening by severe plastic deformation, and alloying to develop precipitation hardening.<sup>3,16,44,91-98</sup>

View Article Online

DOI: 10.1039/D5FD00110B

### 11.3 Grain boundaries and recrystallisation

There is a wide range of grain boundaries with a correspondingly wide range of complex structures and energies even in pure materials and simple alloys.<sup>46,68</sup> Not surprisingly, the complexity of grain-boundary structures is much greater still in multicomponent high-entropy materials. The topological *structural* complexity of accommodating atomic and molecular sites midway between two differently oriented crystals is compounded in a concentrated multicomponent high-entropy solid-solution such as an fcc Cantor alloy or a bcc Senkov alloy by the additional *compositional* complexity of accommodating a large number of different component atoms across the various grain-boundary sites.<sup>3,44</sup> In any polycrystalline Cantor or Senkov alloy, the enormous variety of different local atomic clusters, such as shown in Figures 6 and 7 and Tables 9 and 10 has to be distributed across the many different grain-boundary sites all along the many different grain-boundary planes.<sup>3,44</sup> The resulting complexity and multiplicity of grain boundary structures in multicomponent high-entropy solid-solution single-phase materials is, of course, similar to the complexity and multiplicity discussed previously, arising in the same way for vacancy and dislocation structures in these materials.<sup>3,44</sup>

Direct observation of grain-boundary structures is not easy even in pure materials and simple dilute binary alloys, because of the complex imaging conditions created by the atomic or molecular disorganisation in grain-boundary regions,<sup>46,68</sup> complicating the use of standard high-resolution imaging techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD) and atom probe tomography (AP). And the problems associated with the direct observation of grain-boundary structures are only made worse by the chemical complexity found in multicomponent high-entropy materials. Not surprisingly, therefore, there have been relatively few attempts to investigate multicomponent high-entropy grain-boundary structures by direct observation,<sup>3,16,99</sup> and there have also been relatively few attempts to use atomistic modelling techniques,<sup>3,16,100-102</sup> which are more straightforward technically, but always suffer, as remarked previously, from not



being able to handle anywhere near the very large number of different local atomic clusters that are present in multicomponent high-entropy materials.

View Article Online  
DOI: 10.1039/D5FD00110B

A common method of controlling grain size is by using a mixture of deformation and heat treatment to homogenise and then recrystallise the material.<sup>103,104</sup> There have been quite a few studies of recrystallisation, grain growth and texture in the original equiatomic five-component single-phase fcc Cantor alloy CrMnFeCoNi<sup>105-111</sup> and its equiatomic single-phase fcc quaternary (CrFeCoNi, MnFeCoNi and CrMnCoNi) and ternary (CrFeNi, CrCoNi, MnFeNi, MnCoNi and FeCoNi) subsystems.<sup>110,112-114</sup> Recrystallisation and grain growth in these multicomponent materials are found to be considerably slower than in fcc pure metals and binary alloys, essentially caused by the wide range of local atomic structures and corresponding lattice strains, as shown in Figure 6 and Table 9, slowing the rates of atomic diffusion during heat treatment.<sup>105-107,110,113</sup> Recrystallisation temperatures correspond typically to homologous temperatures relative to the melting point of  $T_r/T_m = 0.6-0.75$ , depending on the alloy composition and the extent of deformation,<sup>113</sup> considerably higher than more typical values in conventional pure metals and binary alloys of  $T_r/T_m = 0.3-0.5$ . The resulting final recrystallised grain sizes are, as a consequence, very small and slow to coarsen, often no larger than 1–5  $\mu\text{m}$  after 1 hour at annealing temperatures of 700–800°C (973–1,073 K)<sup>105-107,110,113</sup> and much smaller than found in fcc nickel,<sup>114</sup> independent of the extent of the initial deformation treatment.<sup>105-107,110,113</sup>

### 11.4 Surfaces and catalysis

Like grain boundaries, the local atomic structure at the surface of a material and the corresponding surface energy depend in a complicated way on the crystallography, orientation and topography of the surface<sup>1,2</sup>. Many important processes and corresponding properties of a material, such as for instance wear, oxidation, corrosion and catalysis, depend intrinsically on its exposure to the external environment and are controlled, therefore, by the details of the variety of local atomic structures at its external surfaces. These processes and associated properties are, not surprisingly, fairly complex even in relatively simple single-phase single-component pure materials<sup>1,2</sup> and, also not surprisingly, become much more complex again in multicomponent high-entropy materials, because of the enormous variety of different local atomic structures,<sup>3,44</sup> as shown in Figures 6 and 7 and Tables 9 and 10. The variety of different atomic structures across the surface of concentrated multicomponent high-entropy metallic and ceramic materials has been shown to lead to considerable enhancements in catalytic efficiency for many different chemical reactions taking place at the surfaces of a variety of different multicomponent high-entropy materials.<sup>115-118</sup> As an example of multicomponent metallic catalysis, five-component FeCoPdIrPt nanoparticles on graphene oxide (FeCoPdIrPt/GO) were shown by Gao et al<sup>119</sup> to operate at a much lower overvoltage





yet with 26 times greater catalytic efficiency for the hydrogen evolution reaction (HER) in a solution of one molar potassium hydroxide (KOH) compared with either single, binary or ternary nanoparticles (such as Fe/GO, CoPd/GO or PdIrPt/GO) or conventional platinised graphite Pt/C. As an example of multicomponent ceramic catalysis, Okejiri et al<sup>120</sup> used Ru<sub>0.13</sub>(BaSrBi)(ZrHfTiFe)O<sub>3</sub> nanoparticles as catalysts for the conversion of CO to CO<sub>2</sub> and achieved faster conversion at lower temperatures compared with BaRuO<sub>3</sub> even though it contains a much higher concentration of ruthenium.

View Article Online  
DOI: 10.1039/D5FD00110B

## 12. What is the electronic structure of high-entropy materials?

In multicomponent high-entropy materials, there are wide and extensive variations in local atomic structure leading to correspondingly wide and extensive variations in local mechanical strain in the lattice.<sup>3,44</sup> And, as just discussed in the previous section, these variations in local mechanical strain affect many important properties, including atomic diffusion and resistance to degradation, dislocation slip and the resulting combination of strength and plasticity, grain boundary motion and recrystallisation, and surface reactivity and catalysis.<sup>3,44</sup> Variations in local mechanical strain are, not surprisingly, mirrored by similar variations in local electronic strain.<sup>3,44</sup> The electronic structure of multicomponent high-entropy materials is, of course, distorted and strained for just the same basic reason as their mechanical structure is distorted and strained, i.e. because of the wide and extensive variations in local atomic structure discussed previously, so that the density of electronic states is not the same at all points throughout the lattice.<sup>3,44</sup>

All of our understanding of the electronic behaviour of crystalline materials comes from being able to find approximate solutions to the time-dependent Schrödinger equation:<sup>121-123</sup>

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{H}\Psi$$

where\*  $i = \sqrt{-1}$ ,  $\hbar = h/2\pi$ ,  $h$  is Planck's constant,  $\Psi(\mathbf{r}_i)$  is the wave function for the set of constituent fundamental particles (electrons, protons and neutrons)  $i$  at positions  $\mathbf{r}_i$  in the material,  $E$  is the energy of the atom and  $\mathcal{H} = \mathcal{T} + \mathcal{V}$  is the Hamiltonian given by:

$$\mathcal{H} = \mathcal{T} + \mathcal{V} = - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{z_i z_j}{(\mathbf{r}_i - \mathbf{r}_j)}$$

\* Notice that  $i$  in the exponential is the imaginary number:  $i = \sqrt{-1}$ , and that elsewhere  $i$  is a label for different electrons:  $\{i\} = i, j, k$  etc.





where  $\mathcal{T}$  and  $\mathcal{V}$  are kinetic and potential energy operators given respectively on the right hand side by the sum of the individual kinetic energies of all the constituent fundamental particles  $i$  and the sum of the individual electrostatic attractions or repulsions of all pairs of constituent fundamental particles  $i$  and  $j$ ,  $m_i$  and  $\mathbf{r}_i$  are the mass and position of the  $i$ 'th particle,  $e$  is the charge on the electron,  $z_i = -1, +1$  and  $0$  for electrons, protons and neutrons respectively, and  $\nabla_i^2 = \partial/\partial x_i^2 + \partial/\partial y_i^2 + \partial/\partial z_i^2$  is the Laplacian operator for the  $i$ 'th particle. Solving this equation requires a large number of simplifying approximations,<sup>121-123</sup> including the following: concentrating on stationary states to remove time-dependence, i.e. solving the simpler time-independent (instead of time-dependent) Schrödinger equation  $E\Psi = \mathcal{H}(\Psi)$ ,<sup>122,123</sup> using the Born-Oppenheimer approximation<sup>124</sup> to concentrate on the valence electrons only by assuming the nucleus and inner electrons of each atom form a relatively massive *clamped* central ion that is effectively fixed in space; using the Hohenberg-Kohn theorem<sup>125</sup> to concentrate exclusively on the ground state of the electrons, with the energy a function then of the electron density  $\rho(\mathbf{r})$  rather than the set of all electron positions  $\{\mathbf{r}_i\}$ , which is why the methodology is often called density functional theory (DFT); treating the valence electrons as independent by re-writing the overall wave function  $\Psi(\mathbf{r}_i) = \prod_i \psi_i(\mathbf{r}_i)$ , i.e. as a product of a set of individual wave functions  $\psi_i(\mathbf{r}_i)$ , one for each valence electron  $i$ ;<sup>122,123</sup> and using Bloch's theorem,<sup>126</sup> to re-write further the set of wave functions  $\psi_i(\mathbf{r}_i)$  as a simpler set of plane waves  $\phi_i(\mathbf{r}_i) = e^{i\mathbf{k}\mathbf{r}_i}$  modulated by a function  $u_i(\mathbf{r}_i) = u_i(\mathbf{r}_i + \mathbf{R})$  which has the periodicity of the crystal lattice:

$$\psi_i(\mathbf{r}_i) = \phi_i(\mathbf{r}_i)u_i(\mathbf{r}_i) = e^{i\mathbf{k}\mathbf{r}_i}u_i(\mathbf{r}_i)$$

where  $\mathbf{k}$  is the wave vector and  $\mathbf{R}$  is any symmetry operation in the crystal lattice. The Bloch theorem<sup>126</sup> enables the stationary set of plane wave functions for the valence electrons to be determined and described within a Brillouin zone that is characteristic of the material and is identical around each atom at each lattice point. Unfortunately, the variation in local atomic structure in multicomponent high-entropy materials disrupts the periodicity of the crystal structure sufficiently to invalidate Bloch's theorem.<sup>3,44</sup> Essentially, the electronic structure, the Brillouin zone and the density of electronic states are all varying so much from lattice site to lattice site that a plane-wave solution to Schrödinger's equation is not realistic.

The mechanical strains in multicomponent high-entropy materials act as pinning points, making atomic diffusion difficult by restricting vacancy migration and dislocation slip. Similarly, the electronic strains in multicomponent high-entropy materials act as scattering points, making electronic motion difficult and leading to relatively low electrical conductivity.<sup>3,44,127-133</sup> Because of the disruption of lattice periodicity described above, it is very difficult to determine more complex electronic



behaviour, and we clearly need more experimental and theoretical studies to explore the resulting electronic, optical and magnetic properties.

View Article Online

DOI: 10.1039/D5FD00110B

### 13. How can we explore multicomponent phase space?

All the early attempts to explore multicomponent phase space and discover new and exciting multicomponent and high entropy materials were undertaken using traditional *ad hoc* investigation methods, i.e. they were pure discovery science, driven largely by trial and error. There have been many attempts since then to use more structured approaches, underpinned by more fundamental scientific theories, and aimed at providing *ab initio* predictions of multicomponent material structures and properties.<sup>3,16,18,134,135</sup> Unfortunately, however, although these attempts have often provided useful information, they have nevertheless been no more than partially successful, mainly because of the enormity of multicomponent phase space and the complexity of the multicomponent materials within it.<sup>3,16,18,134,135</sup> Because of the vast size of multicomponent phase space, we have still only studied relatively few of the trillions of multicomponent materials within it, so our databank of information is quite sparse. And because of the compositional complexity of multicomponent high-entropy materials, our best scientific modelling techniques, even when supported by high-performance computers, are unable to cope adequately with the resulting wide-ranging and extensive variation of local nanostructures contained within them.

The techniques that have been employed to explore multicomponent phase space have included the following: semi-empirical multicomponent Hume-Rothery rules;<sup>3,16,18,134-136</sup> thermodynamic (Calphad) modelling;<sup>3,16,18,137-140</sup> atomistic modelling using density functional theory (DFT), molecular dynamics (MD) and Monte-Carlo (MC) methods;<sup>3,16,18,123,141</sup> and statistical machine learning (ML) algorithms such as support vector machines, decision trees and neural networks.<sup>3,16,18,142-147</sup> Overall, there has been, therefore, quite a large number of detailed studies using multicomponent Hume-Rothery rules,<sup>148-162</sup> thermodynamic modelling,<sup>163-172</sup> atomistic modelling<sup>173-194</sup> and machine learning,<sup>195-212</sup> all aiming to predict the structures and properties of a variety of different multicomponent and high-entropy materials. In summary, all this work shows that valuable information can be obtained, but that the results are somewhat variable and not in general sufficiently accurate for reliable *ab initio* predictions of either the structures or properties of new multicomponent and high-entropy materials. Hume-Rothery methods try to correlate material structures with parameters calculated from the atomic radii, valencies, electronegativities, bulk moduli, melting points and enthalpies and entropies of the component atomic species.<sup>3,16,18,134-136</sup> There are, not surprisingly, clear but rough correlations, with solid solutions being favoured for materials where the components have similar values of atomic radius, valency and electronegativity, and where the heats of mixing are



small and the entropies of mixing are large, but the results are not good enough to guarantee that *ab initio* predictions are correct.<sup>3,18</sup> Calphad-style thermodynamic modelling is based on the fundamental equation discussed previously for the Gibbs free energy of a material:<sup>3,16,18,137-140</sup>

$$G = \sum_i x_i \mu_i^{ss} = \sum_i x_i \mu_i + \Delta G_{mix}$$

$$= \sum_i x_i \mu_i + \Delta H_{mix}(\omega_{ij}, \psi_{ijk}, \chi_{ijkl} \dots) + RT \sum_i x_i \ln x_i - T \Delta S_{mix}^{ss}(\omega_{ij}, \psi_{ijk}, \chi_{ijkl} \dots)$$

The Gibbs free energy can in most cases be calculated only by using estimates for the set of interaction energies  $\omega_{ij}, \psi_{ijk}, \chi_{ijkl} \dots$  etc. that are effectively obtained by extrapolating from known binary mixtures of materials, and this often misses important non-linearities in the behaviour of the large numbers of concentrated and interacting solutes that are present in multicomponent materials. As with multicomponent Hume-Rothery rules, therefore, thermodynamic modelling calculations are helpful but not sufficient to make *ab initio* predictions without first conducting a detailed experimental study of the region of multicomponent phase space of interest.<sup>3,18</sup> Atomistic modelling studies using density functional theory, molecular dynamics or Monte Carlo methods<sup>3,16,18,123,141</sup> perform quantum mechanical, classical mechanical or probabilistic calculations respectively to determine the behaviour of a relatively small number of atoms as a basic calculation unit that is repeated periodically in space. Approximate methods are used to try to build a suitable basic calculation unit that is representative of the material, but it inevitably has far too few atoms to come anywhere near representing the millions of different local nanostructures that are present in multicomponent high-entropy materials, as discussed previously. As with multicomponent Hume-Rothery rules and thermodynamic modelling, therefore, the results are again helpful but insufficient to guarantee successful *ab initio* prediction of structures and properties.<sup>3,18</sup> Machine learning methods can also be useful,<sup>3,16,18,142-147</sup> but are again somewhat limited and not guaranteed to give good *ab initio* predictions, in this case because they work essentially by discovering patterns in existing data, and are, therefore, successful at *interpolating* to predict new information within a known range of materials, but not really successful at *extrapolating* to predict new information in previously unexplored regions of multicomponent phase space.<sup>3,18</sup> Overall, therefore, we can conclude that, in order to achieve successful exploration of multicomponent phase space, there is at present no real alternative to detailed experimental investigation, though this can often be helpfully guided by initial use of multicomponent Hume-Rothery rules, thermodynamic and atomistic modelling and machine-learning calculations.<sup>3,18</sup>

### 13. Conclusions



After a decade and a half of intensive scientific investigation, we have established that multicomponent phase space is very large and contains an enormous number of new materials that have never been made before. Many multicomponent materials are also high-entropy materials, i.e. single-phase solid solutions with random or near-random multiple occupancy of all the lattice sites or one or more of the sublattice sites in the crystal structure. High-entropy materials are based on well-known single-component and binary (and sometimes ternary) compound crystal structures, each with many different compositions, and each occupying a large and complex single-phase field in multicomponent phase space. Increasing the number of components in a material beyond two or three leads to multicomponent high-entropy solid-solution versions of existing single-component and binary and ternary compound structures rather than the development of entirely new multicomponent compound structures with multiple sublattices. The solid-solution single-phase fields in multicomponent phase space are separated by similarly large and complex multiple-phase fields. Some high-entropy materials have been studied intensively, but most have not, and only a few multiple-phase materials have been studied so far. We have not yet mapped out in any detail the extent of the different single-phase and multiple-phase fields. High-entropy materials exhibit large variations in local atomic nanostructure, extending over large distances in the crystal structure, leading to similarly large variations in local mechanical and electronic strain in the lattice. Variations in mechanical strain make it difficult for defects such as vacancies, dislocations and grain boundaries to move around in the high-entropy materials, enhancing their resistance to degradation by exposure to high temperatures, irradiation and corrosion, and increasing their strengths without compromising fracture toughness. We need to develop more detailed experimental and theoretical understanding of the behavior of defects such as vacancies, dislocations, grain boundaries and surfaces within complex multicomponent landscapes of varying local atomic structures and energies in order to explain more fully many of the important thermal and mechanical properties of high-entropy materials. Variations in electronic strain act as scattering centres and make it difficult for electrons to move around, reducing the overall electrical conductivity of high-entropy materials. We need similarly to develop more detailed experimental and theoretical understanding of the behaviour of electrons within complex multicomponent landscapes of varying local atomic structures and energies to explain more fully many of the important electrical, optical and magnetic properties of high-entropy materials. We also need more detailed investigation of the wide variety of different multicomponent multiphase materials. The enormous size of multicomponent phase space and the wide range and extent of different local nanostructures that are present in multicomponent high-entropy materials make it difficult to use thermodynamic modelling, atomistic modelling or machine learning methods with any certainty of successful prediction of new multicomponent high-entropy materials without associated detailed experimental investigation.



## Acknowledgements

The author wishes to thank the Department of Materials at the University of Oxford and the Brunel Centre for Advanced Solidification Technology (BCAST) at Brunel University London for the provision of laboratory and office facilities.

## Conflict of interest

The author has no conflicts of interest. He received laboratory and office support from the Department of Materials, University of Oxford and Brunel Centre for Advanced Casting Technology (BCAST), Brunel University London

## Figure permissions

Fig 1: Author's original drawing and copyright. No permission needed.

Fig 2: Author's original drawing and copyright. No permission needed.

Fig 3: Author's original drawing and copyright. No permission needed.

Fig 4: Author's original drawing and copyright. No permission needed.

Fig 5: Fig 8 from Laurent-Brocq M, Akhatova A, Perrière L, Chebini S, Sauvage X, Leroy E, Champion Y. *Insights into the phase diagram of the CrMnFeCoNi high entropy alloy*. Acta Materialia, 2015, vol 88, pp 355-365.

<https://doi.org/10.1016/j.actamat.2015.01.068>. Permission granted 28/8/25.

Fig 6: Fig 5 from Rost CM, Sachet E, Borman T, Moballegh A, Dickey EC, Hou D, Jones JL, Curtarolo S, Maria JP. *Entropy-stabilized oxides*. Nature Communications, 2015, vol 6, paper number 8485. DOI: [10.1038/ncomms9485](https://doi.org/10.1038/ncomms9485). Open access – no permission required.

Fig 7: Fig 2 from Zhang R, Zhao S, Ding J, Chong Y, Jia T, Ophus C, Asta M, Ritchie RO, Minor AM. *Short-range order and its impact on the CoCrNi medium-entropy alloy*. Nature, 2020, vol 581, pp 283-287. <https://doi.org/10.1038/s41586-020-2275-z>. Permission granted 28/8/25.





Fig 8: Fig 5 from Maiti S, Steurer W. *Structural disorder and its effect on mechanical properties in single-phase TaNbHfZr high-entropy alloy*. Acta Materialia, 2016, vol 106, pp 87-97. <https://doi.org/10.1016/j.actamat.2016.01.018>. Permission granted 28/8/25. View Article Online  
DOI: 10.1039/C5FD00110B

Fig 9: Author's original drawing and copyright. No permission needed.

Fig 10: Author's original drawing and copyright. No permission needed.

Fig 11: Fig 4 from Zou Y, Maiti S, Steurer W, Spolenak R. *Size-dependent plasticity in an Nb<sub>25</sub>Mo<sub>25</sub>Ta<sub>25</sub>W<sub>25</sub> refractory high-entropy alloy*. Acta Materialia, 2014, vol 65, pp 85-97. <https://doi.org/10.1016/j.actamat.2013.11.049>. Permission granted 28/8/25.

Fig 12: Author's original drawing and copyright. No permission needed.

Fig 13: Fig 4 from Okamoto NL, Fujimoto S, Kambara Y, Kawamura M, Chen ZMT, Matsunoshita H, Tanaka K, Inui H, George EP. *Size effect, critical resolved shear stress, stacking fault energy, and solid solution strengthening in the CrMnFeCoNi high-entropy alloy*. Nature Scientific Reports, 2016, vol 6, paper number 35863. DOI: [10.1038/srep35863\(2016\)](https://doi.org/10.1038/srep35863(2016)). Open access – no permission required.

Fig 14: Author's original drawing and copyright.

## References

1. M. F. Ashby, D. R. H. Jones. *Engineering materials* (Pergamon, Oxford, 1986).
2. J. W. Martin. *Materials for engineering*. (Institute of Materials, London, 1996).
3. B. Cantor. *The fundamentals of multicomponent high-entropy materials* (Oxford University Press, Oxford, 2024).
4. B. Cantor, I. T. H. Chang, P. Knight, A. J. B. Vincent. *Microstructural development in equiatomic multicomponent alloys*. Materials Science and Engineering, 2004, vol A375, pp 213-218.
5. A. J. B. Vincent. *A study of three multicomponent alloys*. Undergraduate thesis, University of Sussex, 1981.
6. B. Cantor, K. B. Kim, P. J. Warren. *Novel multicomponent amorphous alloys*. Materials Science Forum (2002), vol 386-388, pp 27-32.
7. K. B. Kim, P. J. Warren, B. Cantor. *Formation of metallic glasses in novel (Ti<sub>33</sub>Zr<sub>33</sub>Hf<sub>33</sub>)(100-x-y)(Ni<sub>50</sub>Cu<sub>50</sub>)(x)Al(y) alloys*. Materials Transactions, 2003, vol 44, pp 411-413.
8. K. B. Kim, P. J. Warren, B. Cantor. *Metallic glass formation in multicomponent (Ti, Zr, Hf, Nb)-(Ni, Cu, Ag)-Al alloys*. Journal of Non-Crystalline Solids, 2003, vol 317, pp 17-22.





9. K. B. Kim, Y. Zhang, P. J. Warren, B. Cantor. *Crystallization behaviour in a new multicomponent TiZrHfNiCuAl metallic glass developed by the equiatomic substitution technique*. Philosophical Magazine, 2003, vol 83, pp 2371-2381.
10. P. K. Huang, J. W. Yeh, T. T. Shun, S. K. Chen. *Multi-principal-element alloys with improved oxidation and wear resistance for thermal spray coating*. Advanced Engineering Materials, 2004, vol 6, pp 74-78.
11. J. W. Yeh, S. K. Chen, S. J. Lin, J. Y. Gan, T. S. Chin, T. T. Shun, C. H. Tsau, S. Y. Chang. *Nanostructured high entropy alloys with multiple principal elements: novel alloy design concepts and outcomes*. Advanced Engineering Materials, 2004, vol 6, pp 299-303.
12. J. W. Yeh, S. K. Chen, J. Y. Gan, S. J. Lin, T. S. Chin, T. T. Shun, C. H. Tsau, S. Y. Chang. *Formation of simple crystal structures in Cu-Co-Ni-Cr-Al-Fe-Ti-V alloys with multiprincipal metallic elements*. Metallurgical and Materials Transactions, 2004, vol 35A, pp 2533-2536.
13. C. Y. Hsu, J. W. Yeh, S. K. Chen, T. T. Shun. *Wear resistance and high-temperature compression strength of fcc Al<sub>0.5</sub>CrFeNiCoCu alloy with boron additions*. Metallurgical and Materials Transactions, 2004, vol 35A, pp 1465-1469.
14. B. Cantor. *The discovery and significance of multicomponent high-entropy alloys*. In: *Fundamental studies of high-entropy materials*, J. Brechtel, P. K. Liaw (eds), (Springer, New York, 2021) chapter 1.
15. J. W. Yeh. *My trip from physics to high entropy materials*. In *Fundamental studies of high-entropy materials*. J. Brechtel, P. K. Liaw (eds), (Springer, New York, 2021) chapter 2.
16. B. S. Murty, J. W. Yeh, S. Ranganathan, P. P. Bhattacharjee. *High-entropy alloys (2<sup>nd</sup> edition)* (Elsevier, Amsterdam, 2019).
17. J. Brechtel, P. K. Liaw (eds). *Fundamental studies of high-entropy materials*. J. Brechtel, P. K. Liaw (eds), (Springer, New York, 2021).
18. B. Cantor. *Exploring multicomponent phase space to discover new materials*. Journal of Phase Equilibria and Diffusion, 2024, vol 45, pp 188-218.
19. *Worldwide guide to equivalent irons and steels (5<sup>th</sup> edition)*. (ASM International, Materials Park Ohio, 2006).
20. *Worldwide guide to equivalent non-ferrous metals and alloys (4<sup>th</sup> edition)*. ASM (International, Materials Park Ohio, 2001).
21. *Annual book of ASTM standards*. (ASTM International, West Conshohocken, Pennsylvania, 2020).
22. K. M. Koh, C. C. Chen. *Principles and techniques in combinatorics*. (World Scientific, Singapore, 1992).
23. R. A. Brualdi. *Introductory combinatorics (5<sup>th</sup> edition)*. (Pearson Prentice Hall, Hoboken NJ, 2010).
24. B. Cantor. *Multicomponent high-entropy Cantor alloys*. Progress in Materials Science, 2021, article number 100754.
25. O. N. Senkov, G. B. Wilks, D. B. Miracle, C. P. Chuang, P. K. Liaw. *Refractory high-entropy alloys*. Intermetallics, 2010, vol 18, pp 1758-1765.

View Article Online

DOI: 10.1039/D5FD00110B



26. O. N. Senkov, D. B. Miracle, K. J. Chaput. *Development and exploration of refractory high entropy alloys — a review*. Journal of Materials Research, 2018, vol 33, pp 3092-3218.
27. D. B. Miracle, M. H. Tsai, O. N. Senkov, V. Soni, R. Banerjee. *Refractory high entropy superalloys*. Scripta Materialia, 2020, vol 187, pp 445-452.
28. *Copper and copper alloys*. (ASM International, Materials Park, Ohio, 2001).
29. H. K. D. H. Bhadeshia, R. W. K. Honeycombe. *Steels: microstructure and properties (4<sup>th</sup> edition)*. (Butterworth-Heinemann, Oxford, 2017).
30. J. D. Musgraves, J. Hu, L. Calvez. *Springer handbook of glass*. (Springer-Nature, Switzerland, 2019).
31. C. R. M. Grovenor. *Microelectronic materials*. (Adam Hilger, Bristol, 1989).
32. L. Mondolfo. *Aluminium alloys: structure and properties (2nd edition)*. (Architectural Press, Taylor and Francis, Oxford, 1979).
33. D. R. Gaskell, D. E. Laughlin. *Introduction to the thermodynamics of materials (6<sup>th</sup> edition)*. (CRC Press, Boca Raton, 2017).
34. M. Hillert. *Phase equilibria, phase diagrams and phase transformations (2<sup>nd</sup> edition)*. (Cambridge University Press, Cambridge, 2008).
35. B. Cantor. *The equations of materials*. (Oxford University Press, Oxford, 2020).
36. B. Cantor. *The thermodynamics of multicomponent high-entropy materials*. Journal of Materials Science, 2024, vol 60, pp 1750-1764.
37. E. J. Pickering, R. Muñoz-Moreno, H. J. Stone, N. G. Jones. *Precipitation in the equiatomic high-entropy alloy CrMnFeCoNi*. Scripta Materialia (2016) vol 113, pp 106-109.
38. F. Otto, A. Diouhy, K. G. Pradeep, M. Kuběnová, D. Raabe, G. Eggeler, E. P. George. *Decomposition of the single-phase high-entropy alloy CrMnFeCoNi after prolonged anneals at intermediate temperatures*. Acta Materialia (2016) vol 112, pp 40-52.
39. J. M. Cowley. *An approximate theory of order in alloys*. Physical Review, 1950, vol 77, pp 669-675.
40. M. Laurent-Brocq, A. Akhatova, L. Perrière, S. Chebini, X. Sauvage, E. Leroy. *Insights into the phase diagram of the CrMnFeCoNi high entropy alloy*. Acta Materialia, 2015, vol 88, pp 355-365.
41. C. M. Rost, E. Sachet, T. Borman, A. Moballeggh, F. C. Dickey, D. Hou, J. L. Jones, S. Curtarolo, J-P. Maria. *Entropy-stabilized oxides*. Nature Communications, 2015, vol 6, paper number 8485.
42. R. Zhang, S. Zhao, J. Ding, Y. Chong, T. Jia, C. Ophus, M. Asta, R. O. Ritchie, A. M. Minor. *Short-range order and its impact on the CoCrNi medium-entropy alloy*. Nature, 2020, vol 581, pp 283-287.
43. S. Maiti, W. Steurer. *Structural disorder and its effect on mechanical properties in single-phase TaNbHfZr high-entropy alloy*. Acta Materialia, 2016, vol 106, pp 87-97.
44. B. Cantor. *Local nanostructure in multicomponent high-entropy materials*. High Entropy Alloys and Materials, 2024, vol 2, pp 277-306.

View Article Online  
DOI: 10.1039/D5FD00110B



45. F. C. Philips. *An introduction to crystallography*. (Wiley, New York, 1973).
46. A. Kelly, K. M. Knowles. *Crystallography and crystal defects*. (Wiley, New York, 2012).
47. N. N. Greenwood, A. Earnshaw. *Chemistry of the elements (2<sup>nd</sup> edition)*. (Butterworth-Heinemann, Oxford, 1997).
48. N. L. Okamoto, K. Yuge, K. Tanaka, H. Inui, E. P. George. *Atomic displacement in the CrMnFeCoNi high entropy alloy: a scaling factor to predict solid solution strengthening*. American Institute of Physics, 2016, vol 6, number 125008.
49. H. S. Oh, D. Ma, G. P. Leyson, B. Grabowski, E. S. Park, F. Körmann, D. Raabe. *Lattice distortions in the FeCoNiCrMn high entropy alloy studied by theory and experiment*. Entropy, 2016, vol 18, pp 321-329
50. H. Song, F. Tian, Q. M. Hu, L. Vitos, Y. Wang, J. Shen, N. Chen. *Local lattice distortions in high-entropy alloys*. Physical Review Materials, 2018, vol 1, number 023404.
51. C. C. Yen, G. R. Huang, Y. C. Huang, H. W. Yeh, D. J. Luo, K. T. Hsieh, E. W. Huang, J. W. Yeh, S. J. Lin, C. C. Wang, C. L. Kuo, S. Y. Chang, Y. C. Lo. *Lattice distortion effect on elastic anisotropy of high entropy alloys*. Journal of Alloys and Compounds, 2020, vol 818, number 152876.
52. L. R. Owen, E. J. Pickering, H. Y. Playford, H. J. Stone, M. G. Tucker, N. G. Jones. *An assessment of the lattice strain in the CrMnFeCoNi high-entropy alloy*. Acta Materialia, 2017, vol 122, pp 11-18.
53. Y. Y. Tan, M. Y. Su, Z. C. Xie, Z. J. Chen, Y. Gong, L. R. Zheng, Z. Shi, G. Mo, Y. Li, L. W. Li, H. Y. Wang, L. H. Dai. *Chemical composition dependent local lattice distortions and magnetism in high entropy alloys*. Intermetallics, 2021, vol 129, paper number 107050.
54. Y. Tong, K. Jin, H. Bei, J. Y. P. Ko, D. C. Pagan, Y. Zhang, F. X. Zhang. *Local lattice distortion in NiCoCr, FeCoNiCr and FeCoNiCrMn concentrated alloys investigated by synchrotron X-ray diffraction*. Materials and Design, 2018, vol 155, pp 1-7.
55. Y. Tong, S. Zhao, K. Jin, H. Bei, J. P. Y. Ko, Y. Zhang, F. X. Zhang. *A comparison study of local lattice distortion in Ni<sub>80</sub>Pd<sub>20</sub> binary alloy and FeCoNiCrPd high entropy alloy*. Scripta Materialia, 2018, vol 156, pp 14-18.
56. H. Ge, F. Tian. *A review of ab initio calculation on lattice distortion in high-entropy alloys*. Journal of Metals, 2019, vol 71, pp 4225-4237.
57. Y. Zou, S. Maiti, W. Steurer, R. Spolenak. *Size-dependent plasticity in an Nb<sub>25</sub>Mo<sub>25</sub>Ta<sub>25</sub>W<sub>25</sub> refractory high-entropy alloy*. Acta Materialia, 2014, vol 65, pp 85-97.
58. W. Guo, W. Dmowski, J. Y. Noh, P. Rack, P. K. Liaw, T. Egami. *Local atomic structure of a high-entropy alloy: an X-ray and neutron scattering study*. Metallurgical and Materials Transactions, 2013, vol 44A, pp 1994-1997.
59. S. Maiti, W. Steurer. *Structural disorder and its effect on mechanical properties in single-phase TaNbHfZr high-entropy alloy*. Acta Materialia, 2016, vol 106, pp 87-97.

View Article Online  
DOI: 10.1039/D5FD00110B



60. R. Abbaschian, L. Abbaschian, R. E. Reed-Hill. *Physical metallurgy principles* (4<sup>th</sup> edition). (Nelson Engineering, 2009).
61. P. Shewmon. *Diffusion in solids* (2<sup>nd</sup> edition). (Springer, New York, 2016).
62. S. L. Thomas, S. Patala. *Vacancy diffusion in multi-principal element alloys: the role of chemical disorder in the ordered lattice*. *Acta Materialia*, 2020, vol 196, pp 144-153.
63. K. Y. Tsai, M. H. Tsai, J. W. Yeh. *Sluggish diffusion in CoCrFeMnNi high-entropy alloy*. *Acta Materialia*, 2013, vol 61, pp 4887-4897.
64. M. Vaidya, K. G. Pradeep, B. S. Murty, G. Wilde, S. V. Divinsky. *Bulk tracer diffusion in CoCrFeNi and CoCrFeMnNi high entropy alloys*. *Acta Materialia*, 2018, vol 146, pp 211-224.
65. M. Vaidya, S. Trubel, B. S. Murty, G. Wilde, S. V. Divinsky. *Ni tracer diffusion in CoCrFeNi and CoCrFeMnNi high entropy alloys*. *Journal of Alloys and Compounds*, 2016, vol 688, pp 994-1001.
66. Q. Li, W. Chen, J. Zhong, L. Zhang, Q. Chen, Z. Liu. *On sluggish diffusion in fcc AlCoCrFeNi high-entropy alloys: an experimental and numerical study*. *Metals*, 2018, vol 8, article number 16.
67. J. Dabrowa, M. Danielewsky. *State-of-the-art diffusion studies in the high entropy alloys*. *Metals*, 2020, vol 10, pp 347-391.
68. W. Cai, W. D. Nix. *Imperfections in crystalline solids*. (Cambridge University Press, Cambridge, 2016).
69. D. Hull, D. J. Bacon. *Introduction to dislocations* (5<sup>th</sup> edition). (Butterworth-Heinemann, Elsevier, Oxford, 2011).
70. Z. Li, S. Zhao, R. O. Ritchie, M. A. Meyers. *Mechanical properties of high-entropy alloys with emphasis on face-centered cubic alloys*. *Progress in Materials Science*, 2019, vol 102, pp 296-345.
71. E. P. George, W. A. Curtin, C. C. Tasan. *High entropy alloys: A focused review of mechanical properties and deformation mechanisms*. *Acta Materialia*, 2020, vol 188, pp 435-474.
72. W. Li, D. Xie, D. Li, Y. Zhang, Y. Gao, P. K. Liaw. *Mechanical behaviour of high-entropy alloys*. *Progress in Materials Science*, 2021, vol 118, paper number 100777.
73. N. L. Okamoto, S. Fujimoto, Y. Kambara, M. Kawamura, Z. M. T. Chen, H. Matsunoshita, K. Tanaka, H. Inui, E. P. George. *Size effect, critical resolved shear stress, stacking fault energy, and solid solution strengthening in the CrMnFeCoNi high-entropy alloy*. *Nature Scientific Reports*, 2016, vol 6, paper number 35863.
74. T. M. Smith, M. S. Hooshmand, B. D. Esser, F. Otto, D. W. McComb, E. P. George, M. Ghazisaeidi, M. J. Mills. *Atomic-scale characterization and modelling of 60° dislocations in a high-entropy alloy*. *Acta Materialia*, 2016, vol 110, pp 352-363.
75. G. Laplanche, A. Kostka, C. Reinhart, J. Hunfeld, G. Eggeler, E. P. George. *Reasons for the superior mechanical properties of medium-entropy CrCoNi compared to high-entropy CrMnFeCoNi*. *Acta Materialia*, 2017, vol 128, pp 292-303.

View Article Online

DOI: 10.1039/D5FD00110B





76. X. D. Xu, P. Liu, Z. Tang, A. Hirata, S. X. Song, T. G. Nieh, P. K. Liaw, C. T. Liu, M. W. Chen. *Transmission electron microscopy characterization of dislocation structure in a face-centred cubic high-entropy alloy  $Al_{0.1}CoCrFeNi$* . *Acta Materialia*, 2018, vol 144, pp 107-115.
77. R. Pasianot, D. Farkas. *Atomistic modeling of dislocations in a random quinary high-entropy alloy*. *Computational Materials Science*, 2020, vol 173, paper number 109366.
78. S. I. Rao, C. Woodward, T. A. Parthasarathy, O. N. Senkov. *Atomistic simulations of dislocation behaviour in a model fcc multicomponent concentrated solid solution alloy*. *Acta Materialia*, 2017, vol 134, pp 188-194.
79. X. Liu, Z. Pei, M. Eisenbach. *Dislocation core structures and Peierls stresses of the high entropy alloy  $NiCoFeCrMn$  and its subsystems*. *Materials and Design*, 2019, vol 180, paper number 107955.
80. J. P. Couzinie, L. Lilensten, Y. Champion, G. Dirras, L. Perrière, I. Guillot. *On the room temperature deformation mechanisms of a  $TiZrHfNbMo$  refractory high-entropy alloy*. *Materials Science and Engineering*, 2015, vol A645, pp 255-263.
81. L. Lilensten, J. P. Couzinie, L. Perrière, A. Hocini, C. Keller, G. Dirras, I. Guillot. *Study of a bcc multi-principal element alloy: tensile and simple shear properties and underlying deformation mechanism*. *Acta Materialia*, 2018, vol 142, pp 131-141.
82. F. Wang, G. H. Balbus, S. Xu, Y. Su, J. Shin, P. F. Rottmann, K. E. Knipling, J. C. Stinville, L. H. Mills, O. N. Senkov, I. J. Beyerlein, T. M. Pollock, D. S. Gianola. *Multiplicity of dislocation pathways in a refractory multiprincipal element alloy*. *Science*, 2020, vol 370, pp 95-101.
83. C. Lee, F. Maresca, R. Feng, Y. Chou, T. Ungar, M. Widom, K. An, J. D. Poplawsky, Y. C. Chou, P. K. Liaw, W. A. Curtin. *Strength can be controlled by edge dislocations in refractory high-entropy alloys*. *Nature Communications*, 2021, paper number 5474.
84. C. Varvenne, A. Luque, W. A. Curtin. *Theory of strengthening in fcc high entropy alloys*. *Acta Materialia*, 2016, vol 118 pp 164-176.
85. C. Varvenne, G. P. M. Leyson, M. Ghazisaeidi, W. A. Curtin. *Solute strengthening in random alloys*. *Acta Materialia* 2017, vol 124 pp 660-683.
86. C. Varvenne, W. A. Curtin. *Strengthening of high entropy alloys by dilute solute additions:  $CoCrFeNiAl_x$  and  $CoCrFeNiMnAl_x$  alloys*. *Scripta Materialia*, 2017, vol 138 pp 92-5.
87. S. Sohn, Y. Liu, J. Liu, P. Gong, S. Prades-Rodel, A. Blatter, B. E. Scanlon, C. C. Broadbridge, J. Schroers. *Noble metal high entropy alloys*. *Scripta Materialia* 2017, vol 126, pp 29-32.
88. B. Yin, W. A. Curtin. *First-principles-based prediction of yield strength in the  $RhIrPdPtNiCu$  high-entropy alloy*. *NPJ Computational Materials*, 2019, vol 5, paper number 14.

View Article Online  
DOI: 10.1039/D5FD00110B



89. F. Maresca, W. A. Curtin. *Theory of screw dislocation strengthening in random bcc alloys from dilute to high-entropy alloys*. Acta Materialia, 2020, vol 182, pp 144-162.
90. B. Gludovatz, A. Hohenwarter, D. Catoor, E. H. Chang, E. P. George, R. O. Ritchie. *A fracture-resistant high-entropy alloy for cryogenic applications*. Science, 2014, vol 345, pp 1153–1158.
91. Z. Li, S. Zhao, R. O. Ritchie, M. A. Meyers. *Mechanical properties of high-entropy alloys with emphasis on face-centered cubic alloys*. Progress in Materials Science, 2019, vol 102, pp 296-345.
92. E. P. George, W. A. Curtin, C. C. Tasan. *High entropy alloys: A focused review of mechanical properties and deformation mechanisms*. Acta Materialia, 2020, vol 188, pp 435-474.
93. W. Li, D. Xie, D. Li, Y. Zhang, Y. Gao, P. K. Liaw. *Mechanical behaviour of high-entropy alloys*. Progress in Materials Science, 2021, vol 118, paper number 100777.
94. O. N. Senkov, D. B. Miracle, K. J. Chaput, J. P. Couzinie. *Development and exploration of refractory high entropy alloys – a review*. Journal of Materials Research, 2018, vol 33, pp 3092-3128.
95. D. B. Miracle, M. H. Tsai, O. N. Senkov, V. Soni, R. Banerjee. *Refractory high entropy superalloys*. Scripta Materialia, 2020, vol 187, pp 445-452.
96. J. Zhou, Y. Cheng, Y. Chen, X. Liang. *Composition design and preparation process of refractory high-entropy alloys: a review*. International Journal of Refractory Metals and Hard Materials, 2022, vol 105, paper number 105836.
97. X. Ren, Y. Li, Y. Qi, B. Wang. *Review on preparation technology and properties of refractory high entropy alloys*. Materials, 2022, vol 15, paper number 2931.
98. B. Chen, L. Zhuo. *Latest progress on refractory high entropy alloys: composition, fabrication, post processing, performance, simulation and prospect*. International Journal of refractory Metals and Hard Materials, 2023, vol 110, paper number 105993.
99. Q. Lin, X. An, H. Liu, Q. Tang, P. Dai, X. Liao. *In-situ high-resolution transmission electron microscopy investigation of grain boundary dislocation activities in a nanocrystalline CrMnFeCoNi high-entropy alloy*. Journal of Alloys and Compounds, 2017, vol 709, pp 802-807.
100. P. Wynblatt, D. Chatain. *Modeling grain boundary and surface segregation in multicomponent high-entropy alloys*. Physical Review Materials, 2019, vol 3, paper number 054004.
101. D. Farkas. *Grain boundary structure in high-entropy alloys*. Journal of Materials Science, 2020, vol 55, pp 9173-9183.
102. H. Lee, M. Shabani, G. J. Pataky, F. Abdeljawad. *Tensile deformation behavior of twist grain boundaries in CoCrFeMnNi high entropy bicrystals*. Nature Scientific Reports, 2021, vol 11, paper number 428.
103. R. D. Doherty, D. A. Hughes, F. J. Humphreys, J. J. Jonas, D. J. Jensen, M. E. Kassner, W. E. King, T. R. McNelley, H. J. McQueen, A. D. Rollett.

View Article Online  
DOI: 10.1039/D5FD00110B





*Current issues in recrystallization: a review*. Materials Science and Engineering, 1997, vol A238, pp 219-274.

View Article Online

DOI: 10.1039/D5FD00110B

104. J. Humphreys, G. S. Rohrer, A. Rollett. *Recrystallization and related annealing phenomena* (3<sup>rd</sup> edition). (Elsevier, Amsterdam, 2017).
105. W. H. Liu, Y. Wu, J. ¥. He, T. G. Nieh, Z. P. Lu. *Grain growth and the Hall-Petch relationship in a high-entropy FeCrNiCoMn alloy*. Scripta Materialia, 2013, vol 68, pp 526-529.
106. P. P. Bhattacharjee, G. D. Sathiaraj, M. Zaid, J. R. Gatti, C. Lee, C. W. Tsai, J. Y. Yeh. *Microstructure and texture evolution during annealing of equiatomic CoCrFeMnNi high-entropy alloy*. Journal of Alloys and Compounds, 2014, vol 587, pp 544-552.
107. F. Otto, N. L. Hanold, E. P. George. *Microstructural evolution after thermomechanical processing in an equiatomic single-phase CoCrFeMnNi high-entropy alloy with special focus on twin boundaries*. Intermetallics, 2014, vol 54, pp 39-48.
108. G. Laplanche, O. Horst, G. Eggeler, E. P. George. *Microstructural evolution of a CoCrFeMnNi alloy after swaging and annealing*. Journal of Alloys and Compounds, 2015, vol 647, pp 548-557.
109. G. D. Sathiaraj, P. P. Bhattacharjee. *Analysis of microstructure and microtexture during grain growth in low stacking fault energy equiatomic CoCrFeMnNi high entropy and Ni-60wt%Co alloys*. Journal of Alloys and Compounds, 2015, vol 637, pp 267-276.
110. B. R. Chen, A. C. Yeh, J. W. Yeh. *Effect of one-step recrystallization on the grain boundary evolution of CoCrFeMnNi high entropy alloy and its subsystems*. Nature Scientific Reports, 2016, vol 6, paper number 22306.
111. J. Gu, S. Ni, Y. Liu, M. Song. *Regulating the strength and ductility of a cold rolled FeCrCoMnNi high-entropy alloy via annealing treatment*. Materials Science and Engineering, 2019, vol A755, pp 289-294.
112. P. Shiyamoorthi, P. Asghari-Rad, J. W. Bae, H. S. Kim. *Fine tuning of tensile properties in CrCoNi medium entropy alloy through cold rolling and annealing*. Intermetallics, 2019, vol 113, paper number 106578.
113. Z. Wu, H. Bei, F. Otto, G. M. Pharr, E. P. George. *Recovery, recrystallization, grain growth and phase stability of a family of fcc-structured multicomponent equiatomic solid solution alloys*. Intermetallics, 2014, vol 46, pp 131-140.
114. Z. Yang, F. He, Q. Wu, K. Zhang, D. Cui, B. Guo, B. Han, J. Li, J. Wang, Z. Wang. *Distinct recrystallization kinetics in NiCoCrFe-based single-phase high-entropy alloys*. Metallurgical and Materials Transactions, 2021, vol A52, pp 3799-3810.
115. Y. Zhang, D. Wang, S. Wang. *High-entropy alloys for electrocatalysis: design, characterization and applications*. Small, 2022, vol 18, paper number 2104339.



116. K. Kusada, M. Mukoyoshi, D. Wu, H. Kitagawa. *Chemical synthesis, characterization and properties of multi-element nanoparticles*. *Angewandte Chemie*, 2022, vol 61, paper number 09616. View Article Online  
DOI: 10.1039/D5FD00110B
117. H. Li, J. Lai, Z. Li, L. Wang. *Multi-sites electrocatalysis in high-entropy alloys*. *Advanced Functional Materials*, 2021, vol 31, paper number 2106715.
118. B. Wang, Y. Yao, X. Yu, C. Wang, C. Wu, Z. Zou. *High entropy alloys: from theory to experiment*. *Journal of Materials Chemistry A*, 2021, vol 9, pp 19410-19438.
119. S. Gao, S. Hao, Z. Huang, Y. Yuan, S. Han, L. Lei, X. Zhang, R. Shahbazian-Yassar, J. Lu. *Synthesis of high-entropy alloy nanoparticles on supports by the fast moving bed pyrolysis*. *Nature Communications*, 2020, vol 11, paper number 2016.
120. F. Okejiri, Z. Zhang, J. Liu, M. Liu, S. Yang, S. Dai. *Room-temperature synthesis of high-entropy perovskite oxide nanoparticle catalysts through ultrasonication-based method*. *Chemsuschem*, 2019, vol 13, pp 111-115.
121. C. Kittel. *Introduction to solid state physics (2<sup>nd</sup> edition)*. (Wiley, New York, 1957).
122. A. P. Sutton AP. *Electronic structure of materials*. (Oxford University Press, Oxford 1993).
123. Z. H. Barber (ed). *Introduction to materials modelling*. (Maney, London, 2005).
124. M. Born, R. Oppenheimer. *Zur quantentheorie der molekeln [On the quantum theory of molecules]*. *Annalen der Physik*, 1927, vol 84, pp 457-484.
125. P. Hohenberg, W. Kohn. *Inhomogeneous electron gas*. *Physical Review B*, 1964, vol 136, pp 864-871.
126. F. Bloch. *Über die quantenmechanik der elektronen in kristallgittern [On the quantum mechanics of electrons in crystal lattices]*. *Zeitschrift für Physik*, 1928, vol 52, pp 555-600.
127. P. Bag, Y. C. Su, Y. K. Kuo, Y. C. Lai, S. K. Wu. *Physical properties of face-centred cubic structured high-entropy alloys: effects of NiCo, NiFe and NiCoFe alloying with Mn, Cr and Pd*. *Physical Review Materials*, 2021, vol 5, paper number 085003.
128. G. D. Samolyuk, S. Mu, A. F. May, B. C. Sales, S. Wimmer, S. Mankovsky, H. Ebert, G. M. Stocks. *Temperature-dependent electronic transport in concentrated solid solutions of the 3d-transition metals Ni, Fe, Co and Cr from first principles*. *Physical Review B*, 2018, vol 98, paper number 165141.
129. S. Mu, G. D. Samolyuk, S. Wimmer, M. C. Tropicovsky, S. Khan, S. Mankovsky, H. Ebert, G. M. Stocks. *Uncovering electron scattering mechanisms in NiFeCoCrMn derived concentrated solid solution and high entropy alloys*. *NPJ Computational Materials*, 2019, vol 5, pp 1-8.
130. K. Jin, B. C. Sales, G. M. Stocks, G. D. Samolyuk, M. Daene, W. J. Weber, Y. Zhang, H. Bei. *Tailoring the physical properties of Ni-based single-phase*



*equiatomic alloys by modifying the chemical complexity*. Scientific Reports, 2016, vol 6, paper number 20159.

View Article Online

DOI: 10.1039/D5FD00110B

131. Y. Mu, H. Liu, Y. Liu, X. Zhang, Y. Jiang, T. Dong. *An ab initio and experimental studies of the structure, mechanical parameters and state density on the refractory high-entropy alloy systems*. Journal of Alloys and Compounds, 2017, vol 714, pp 668-680.
132. C. Chang, H. Zhang. *First-principles calculations to investigate elastic and thermodynamic properties of FeAlNi<sub>x</sub>CrMn quaternary alloys*. Journal of Materials Research and Technology, 2022, vol 18, pp 1322-1332.
133. Y. Tong, L. Bai, X. Liang, Y. Chen, Z. Zhang, J. Liu, Y. Li, Y. Hu. *Influence of alloying elements on mechanical and electronic properties of NbMoTaW<sub>X</sub> (X = Cr, Zr, V, Hf and Re) refractory high entropy alloys*. Intermetallics, 2020, vol 126, paper number 106928.
134. D. B. Miracle, O. N. Senkov. *A critical review of high-entropy alloys and related concepts*. Acta Materialia, 2017, vol 122, pp 448-511.
135. V. K. Soni, S. Sanyal, K. Raja Rao, S. K. Sinha. *A review on phase prediction in high entropy alloys*. Journal of Mechanical Engineering Science, 2021, vol 235, pp 6268-6286.
136. U. Mizutani. *Hume-Rothery rules for structurally complex alloy phases*. (CRC Press, Boca Raton, 2019).
137. C. Li, Y. Yuan, F. Li, Q. Wei, Y. Huang. *Modification and verification of Miedema model for predicting thermodynamic properties of binary precipitates in multi-element alloys*. Physica B: Condensed Matter, 2022, vol 627, article number 413540.
138. L. Kaufman, H. Bernstein. *Computer calculations of phase diagrams*. (Academic Press, New York 1970).
139. N. Saunders, A. P. Miodownik. *Calphad: calculation of phase diagrams: a comprehensive guide*. (Pergamon Elsevier, Oxford, 1998).
140. H. L. Lukas, S. G. Fries, B. Sundman. *Computational thermodynamics*. (Cambridge University Press, Cambridge, 2007).
141. F. Giustino. *Materials modelling using density functional theory*. Oxford University Press, Oxford, 2014.
142. L. Qiao, Y. Liu, J. Zhu. *A focused review on machine learning aided high-throughput methods in high entropy alloy*. Journal of Alloys and Compounds, 2021, vol 877, paper number 160295.
143. G. L. W. Hart, T. Mueller, C. Toher, S. Curtarolo. *Machine learning for alloys*. Nature Reviews Materials, 2021, vol 6, pp 730-755.
144. X. Liu, P. Xu, J. Zhao, W. Lu, M. Li, G. Wang. *Material machine learning for alloys: applications, challenges and perspectives*. Journal of Alloys and Compounds, 2022, vol 921, papernumber 165984.
145. A. Burkov. *The hundred page machine learning book*. Andriy Burkov, 2019.
146. P. Flach. *Machine learning: the art and science of algorithms that make sense of data*. Cambridge University Press, Cambridge, 2012.



147. S. Russell, P. Norvig. *Artificial intelligence: a modern approach* (4<sup>th</sup> edition). Pearson Education, Harlow, 2022, section V: machine learning, pp 669-873.
148. Y. Zhang, Y. J. Zhou, J. P. Lin, G. L. Chen, P. K. Liaw. *Solid-solution phase formation rules for multi-component alloys*. *Advanced Engineering Materials*, 2008, vol 10, pp 534-538.
149. X. Yang, Y. Zhang. *Prediction of high-entropy stabilized solid-solution in multi-component alloys*. *Materials Chemistry and Physics*, 2012, vol 132, pp 233-238.
150. Y. Zhang, X. Yang, P. K. Liaw. *Alloy design and properties optimization of high-entropy alloys*. *Journal of Metals*, 2012, vol64, pp 830-838.
151. S. Guo, Q. Hu, C. Ng, C. T. Liu. *More than entropy in high-entropy alloys: forming solid solutions or amorphous phase*. *Intermetallics*, 2013, vol 41, pp 96-103.
152. A. Takeuchi, K. Amiya, T. Wada, K. Yubuta, W. Zhanb, A. Makino. *Entropies in alloy design for high entropy and bulk glassy alloys*. *Entropy*, 2013, vol 15, pp 3810-3821.
153. M. X. Ren, B. X. Li, H. Z. Fu. *Formation condition of solid solution type high-entropy alloy*. *Transactions of the Nonferrous Metals Society of China (English Edition)*, 2013, vol 23, pp 991-995.
154. M. G. Poletti, L. Battezzati. *Electronic and thermodynamic criteria for the occurrence of high entropy alloys in metallic systems*. *Acta Materialia*, 2014, vol 75 297-306.
155. G. A. Salishchev, M. A. Tikhonovsky, D. G. Shaysultanov, N. D. Stepanov, A. V. Kuznetsov, I. V. Kolodiy, A. S. Tortika, O. N. Senkov. *Effect of Mn and V on structure and mechanical properties of high-entropy alloys based on CoCr- FeNi system*. *Journal of Alloys and Compounds*, 2014, vol 591, pp 11-21.
156. Z. S. Nong, J. C. Zhu, Y. Cao, X. W. Yang, Z. H. Lai, Y. Liu. *Stability and structure prediction of cubic phase in as cast high entropy alloys*. *Materials Science and Technology*, 2014, vol 30 363-369.
157. S. Guo. *Phase selection rules for cast high entropy alloys: an overview*, *Materials Science and Technology*, 2015, vol 31, 1223-1230.
158. Z. Wang, Y. Huang, Y. Yang, J. Wang, C. T. Liu. *Atomic size effect and solid solubility of multicomponent alloys*. *Scripta Materialia*, 2015, vol 94, pp 28-31.
159. Y. F. Ye, Q. Wang, J. Lu, C. T. Liu, Y. Yang. *The generalized thermodynamic rule for phase selection in multicomponent alloys*. *Intermetallics*, 2015, vol 59, pp 75-80.
160. D. J. M. King, S. C. Middleburgh, A. G. Mc Gregor, M. B. Cortie. *Predicting the formation and stability of single phase high-entropy alloys*. *Acta Materialia*, 2016, vol 104, pp 172-179.
161. O. N. Senkov, D. B. Miracle. *A new thermodynamic parameter to to predict formation of solid solutions or intermetallic phases in high entropy alloys*. *Journal of Alloys and Compounds*, 2016, vol 658, pp 603-607.





162. I. T. Caraballo, P. E. J. Rivera-Diaz-del-Castillo. *A criterion for the formation of high entropy alloys based on lattice distortion*. *Intermetallics*, 2016, vol 71, pp 76-87. View Article Online  
DOI: 10.1039/D5FD00110B
163. K. C. Hsieh, C. F. Yu, W. T. Hsieh, W. R. Chiang, J. S. Ku, J. H. Lai, C. P. Tu, C. C. Yang. *The microstructure and phase equilibrium of new high performance high-entropy alloys*. *Journal of Alloys and Compounds*, 2009, volume 483, pp 209-212.
164. C. Huang, Y. Zhang, J. Shen, R. Vilar. *Thermal stability and oxidation resistance of laser clad TiVCrAlSi high entropy alloy coatings on Ti-6Al-4V alloy*. *Surface and Coatings Technology*, 2011, volume 206, pp 1389-1395.
165. O. N. Senkov, F. Zhang, J. D. Miller. *Phase composition of a CrMoNbTaTiZr high entropy alloy: comparison of experimental and simulated data*. *Entropy*, 2013, volume 15, pp 3796-3809.
166. M. C. Gao, D. E. Alman. *Searching for next single-phase high-entropy alloy compositions*. *Entropy*, 2013, volume 15, pp 4504-4519.
167. J. E. Saal, I. S. Berglund, J. T. Sebastian, P. K. Liaw, G. B. Olson. *Equilibrium high entropy alloy phase stability from experiments and thermodynamic modeling*. *Scripta Materialia*, 2018, vol 146, pp 5-8.
168. T. T. Shun, Y. C. Du. *Microstructure and tensile behaviors of fcc Al<sub>0.3</sub>CoCrFeNi high entropy alloy*. *Journal of Alloys and Compounds*, 2009, vol 479, pp 157-160.
169. Y. F. Kao, S. K. Chen, T. J. Chen, P. C. Chu, J. W. Yeh, S. J. Lin. *Electrical, magnetic and Hall properties of Al<sub>x</sub>CoCrFeNi high-entropy alloys*. *Journal of Alloys and Compounds*, 2011, vol 509, pp 1607-1614.
170. W. R. Wang, W. L. Wang, J. W. Yeh. *Phases, microstructure and mechanical properties of Al<sub>x</sub>CoCrFeNi high-entropy alloys at elevated temperatures*. *Journal of Alloys and Compounds*, 2014, vol 589, pp 143-152.
171. Q. Tang, Y. Huang, H. Cheng, X. Liao, T. G. Langdon, P. Dai. *The effect of grain size on the annealing-induced phase transformation in an Al<sub>0.3</sub>CoCrFeNi high entropy alloy*. *Materials Design*, 2016, vol 105, pp 381-385.
172. F. He, Z. Wang, Q. Wu, J. Li, J. Wang, C. T. Liu. *Phase separation of metastable CoCrFeNi high entropy alloy at intermediate temperatures*. *Scripta Materialia*, 2017, vol 126, pp 15-19.
173. F. Tian. *A review of solid-solution models of high-entropy alloys based on ab initio calculations*. *Frontiers in Materials*, 2017, vol 4, paper number 36.
174. F. Tian, Y. Wang, D. L. Irving, L. Vitos. *Applications of coherent potential approximations to HEAs*. In: *High-entropy alloys: fundamentals and applications* eds M. C. Gao, J. W. Yeh, P. K. Liaw, Y. Zhang. Springer International, Switzerland, 2016, ch 9, pp 299-332.
175. M. C. Gao, C. Niu, C. Jiang, D. L. Irving. *Applications of special quasi-random structures to high-entropy alloys*. In: *High-entropy alloys: fundamentals and applications* eds M. C. Gao, J. W. Yeh, P. K. Liaw, Y. Zhang. Springer International, Switzerland, 2016, ch 10, pp 333-368.





176. D. Ma, B. Grabowski, F. Körmann, J. Neugebauer, D. Raabe. *Ab initio thermodynamics of the CoCrFeMnNi high entropy alloy: importance of entropy contributions beyond the configurational one*. Acta Materialia, 2015, vol 100, pp 90-97.
177. X. Sun, H. Zhang, S. Lu, X. Ding, Y. Wang, L. Vitos. *Phase selection rule for Al-doped CrMnFeCoNi high-entropy alloys from first principles*. Acta Materialia 2017, vol 140, pp 366-374.
178. J. Y. He, W. H. Liu, H. Wang, Y. Wu, X. J. Liu, T. G. Nieh, Z. P. Lu. *Effects of Al addition on structural evolution and tensile properties of the FeCoNiCrMn high-entropy alloy system*. Acta Materialia 2014, vol 62, pp 105-113.
179. F. Y. Tian, L. Delczeg, N. X. Chen, L. K. Varga, J. Shen, L. Vitos. *Structural stability of NiCoFeCrAl<sub>x</sub> high-entropy alloy from ab initio theory*. Physical Review B, 2013, vol 88, paper number 085128.
180. S. Yang, Y. Zhong. *Ab initio modeling of fcc FeCoCrNi high entropy alloys with full composition range*. Journal of Phase Equilibria and Diffusion, 2021, vol 42, pp 656-672.
181. S. Yang, G. Liu, Y. Zhong. *Revisit the VEC criterion in high entropy alloys (HEAs) with high throughput ab initio calculations: a case study with AlCoCrFeNi system*. Journal of Alloys and Compounds, 2022, vol 916, paper number 165477.
182. Guo S, Ng C, Lu J, Liu C. *Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys*. Journal of Applied Physics, 2011, vol 109, paper number 103505.
183. F. Tian, L. K. Varga, N. Chen, J. Shen, L. Vitos. *Ab initio design of elastically isotropic TiZrNbMoV<sub>x</sub> high-entropy alloys*. Journal of Alloys and Compounds, 2014, vol 599, pp 19-25.
184. S. W. McAlpine, J. V. Logan, M. P. Short. *Predicting single phase stability and segregation in the NbMoTaTi-(W,V) high entropy alloy system with the vacancy exchange potential*. Scripta Materialia, 2021, vol 191, pp 29-33.
185. Q. Zhao, J. Li, Q. Fang, H. Feng. *Effect of Al solute concentration on mechanical properties of Al<sub>x</sub>FeCuCrNi high-entropy alloys: a first principles study*. Physica B: Condensed Matter, 2019, vol 566, pp 30-37.
186. C. Niu, A. J. Zaddach, C. C. Koch, D. L. Irving. *First principles exploration of near-equiatomic NiFeCrCo high entropy alloys*. Journal of Alloys and Compounds, 2016, vol 672, pp 510-520.
187. H. Song, F. Tian, Q. M. Hu, L. Vitos, Y. Wang, J. Shen, N. Chen. *Local lattice distortion in high-entropy alloys*. Physical Review Materials, 2017, vol 1, paper number 023404.
188. M. Karabin, W. R. Mondal, A. Östlin, W. G. D. Ho, V. Dobrosavljevic, K. M. Tam, H. Terletska, L. Chioncel, Y. Wang, M. Eisenbach. *Ab initio approaches to high-entropy alloys: a comparison of CPA, SQS and supercell methods*. Journal of Materials Science, 2022, vol 57, pp 10677-10690.

View Article Online

DOI: 10.1039/D5FD00110B



189. S. M. Chen, Z. J. Ma, S. Qiu, L. J. Zhang, S. Z. Zhang, R. Yang, Q. M. Hu. *Phase decomposition and strengthening in HfNbTaTiZr high entropy alloy from first-principles calculations*. Acta Materialia, 2022, vol 225, paper number 117582.
190. F. Biermair, V. I. Razumovskiy, G. Ressel. *Influence of alloying on thermodynamic properties of AlCoCrFeNiTi high entropy alloys from DFT calculations*. Computational Materials Science, 2022, vol 202, paper number 110952.
191. S. San, Y. Tong, H. Bei, B. Kombariah, Y. Zhang, W. Y. Ching. *First-principles calculation of lattice distortion in four single phase high entropy alloys with experimental validation*. Materials and Design, 2021, vol 209, paper number 110071.
192. S. Liu, P. Cao, D. Y. Lin, F. Tian. *Stability of L2<sub>1</sub> (NiM)<sub>2</sub>TiAl (M=Co, Fe) in high-entropy alloys*. Journal of Alloys and Compounds, 2018, vol 764, pp 650-655.
193. S. Wang, S. Chen, Y. Jia, H. Hu, H. Huang, Z. Yang, A. Dong, G. Zhu, D. Wang, D. Shu, F. Tian, Y. Dai, B. Sun. *Fcc-L1<sub>2</sub> ordering transformation in equimolar FeCoNiV multi-principal element alloy*. Materials and Design, 2019, vol 168, paper number 107648.
194. R. Rytsev, V. Gaviko, S. Estemirova, E. Sterkhov, L. Cherepanova, D. Yagodin, N. Chetkatchev, N. Dubinin, S. Uporov. *Laves formation in high entropy alloys*. Metals, 2021, vol 11, paper number 1962.
195. N. Islam, W. Huang, H. L. Zhuang. *Machine learning for phase selection in multi-principal element alloys*. Computational Materials Science, 2018, vol 150, pp 230-235.
196. R. Bobbili, B. Ramakrishna, V. Madhu. *Development of machine learning based models for design of high entropy alloys*. Materials Technology, 2022, vol 37, paper number 2046930.
197. W. Huang, P. Martin, H. L. Zhuang. *Machine learning phase prediction of high-entropy alloys*. Acta Materialia, 2019, vol 169, pp 225-236.
198. P. Mandal, A. Choudhury, A. B. Mallick, M. Ghosh. *Phase prediction in high entropy alloys by various machine learning modules using thermodynamic and configurational parameters*. Metals and Materials International, 2022.
199. Y. Yan, D. Lu, K. Wang. *Accelerated discovery of single-phase refractory high entropy alloys assisted by machine learning*. Computational Materials Science, 2021, vol 199, paper number 110723.
200. A. E. Nassar, A. M. Mullis. *Rapid screening of high entropy alloys using neural networks and constituent elements*. Computational Materials Science, 2021, vol 199, paper number 110755.
201. K. Kaufmann, K. S. Vecchio. *Searching for high entropy alloys: machine learning approach*. Acta Materialia, 2020, vol 198, pp 178-222.
202. U. K. Jaiswal, Y. V. Krishna, M. R. Rahul, G. Phanikumar. *Machine learning-enabled identification of new medium to high entropy alloys with solid*

View Article Online  
DOI: 10.1039/D5FD00110B



*solution phases*. Computational Materials Science, 2021, vol197, paper number 110623.

View Article Online

DOI: 10.1039/D5FD00110B

203. T. Wen, B. Ye, H. Liu, S. Ning, C. Z. Wang, Y. Chu. *Formation criteria for binary metal diboride solid solutions established through combinatorial methods*. Journal of the American Ceramic Society, 2019, vol 103, pp 3338-3348.
204. K. Kaufmann, D. Maryanovsky, W. M. Mellor, C. Zhu, A. S. Rosengarten, T. J. Harrington, C. Oses, C. Toher, S. Curtarolo, K. S. Vecchio. *Discovery of high-entropy ceramics via machine learning*. NPJ Computational Materials, 2020, vol 6, paper number 42.
205. F. Z. Dai, B. Wen, Y. Sun, H. Xiang, Y. Zhou. *Theoretical prediction on thermal and mechanical properties of high entropy (ZrHfTiNbTa)C by deep learning potential*. Journal of Materials Science and Technology, 2020, vol 43, pp 168-174.
206. F. Z. Dai, Y. Sun, B. Wen, H. Xiang, Y. Zhou. *Temperature dependent thermal and elastic properties of high entropy (TiZrHfNbTa)B<sub>2</sub>: molecular dynamics simulation by deep learning potential*. Journal of Materials Science and Technology, 2021, vol 72, pp 8-15.
207. W. M. Mellor, K. Kaufmann, O. F. Dippo, S. D. Figuera, G. D. Schrader, K. S. Vecchio. *Development of ultrahigh-entropy ceramics with tailored oxidation behavior*. Journal of the European Ceramic Society, 2021, vol 41, pp 5791-5800.
208. J. Zhang, B. Xu, Y. Xiong, S. Ma, Z. Wang, Z. Wu, S. Zhao. *Design high-entropy carbide ceramics from machine learning*. NPJ Computational Materials, 2022, vol 8, paper number 5.
209. R. Mitra, A. Bajpai, K. Biswas. *Machine learning based approach for phase prediction in high entropy borides*. Ceramics International, 2022, vol 48, pp 16695-16706.
210. Y. J. Chang, C. Y. Jui, W. J. Lee, A. C. Yeh. *Prediction of the composition and hardness of high-entropy alloys by machine learning*. Journal of Metals, 2019, vol 71, pp 3433-3442.
211. C. W. Wen, Y. Zhang, C. Wang, D. Xue, Y. Bai, S. Antonav, L. Dai, T. Lookman, Y. Su. *Machine learning assisted design of high entropy alloys with desired property*. Acta Materialia, 2019, vol 170, pp 109-117.
212. C. Wen, C. Wang, Y. Zhang, S. Antonov, D. Xue, T. Lookman, Y. Su. *Modeling solid solution strengthening in high entropy alloys using machine learning*. Acta Materialia, 2021, vol 212, paper number 116917.



## Data availability

[View Article Online](#)  
DOI: 10.1039/D5FD00110B

No primary research results, software or code have been included and no new data were generated or analysed as part of this manuscript

