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Non-equiatomic high entropy alloys: Approach towards rapid alloy screening and property-oriented design

K.G. Pradeep [a,b], C.C. Tasan [a,*], M.J. Yao [a], Y. Deng [a,c], H. Springer [a], D. Raabe [a,*]

[a] Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-str.1, 40237 Düsseldorf, Germany
[b] Materials Chemistry, RWTH Aachen University, Kopernikusstr.10, 52074 Aachen, Germany
[c] Department of Engineering Design and Materials, Norwegian University of Science and Technology, No-7491 Trondheim, Norway

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ABSTRACT

The high entropy alloy (HEA) concept has triggered a renewed interest in alloy design, even though some aspects of the underlying thermodynamic concepts are still under debate. This study addresses the shortcomings of this alloy design strategy with the aim to open up new directions of HEA research targeting specifically non-equiatomic yet massively alloyed compositions. We propose that a wide range of massive single phase solid solutions could be designed by including non-equiatomic variants. It is demonstrated by introducing a set of novel non-equiatomic multi-component CoCrFeMnNi alloys produced by metallurgical rapid alloy prototyping. Despite the reduced configurational entropy, detailed characterization of these materials reveals a strong resemblance to the well-studied equiatomic single phase HEA: The microstructure of these novel alloys exhibits a random distribution of alloying elements (confirmed by Energy-Dispersive Spectroscopy and Atom Probe Tomography) in a single face-centered-cubic phase (confirmed by X-ray Diffraction and Electron Backscatter Diffraction), which deforms through planar slip (confirmed by Electron-Channeling Contrast Imaging) and leads to excellent ductility (confirmed by uniaxial tensile tests). This approach widens the field of HEAs to non-equiatomic multi-component alloys since the concept enables to tailor the stacking fault energy and associated transformation phenomena which act as main mechanisms to design useful strain hardening behavior.

1. Introduction

The High Entropy Alloy (HEA) concept has attracted significant interest in recent years due to the novelty of the underlying alloy design principle and the promising mechanical properties of the massive solid solution microstructures [1,2]. In general, the concept inherits the idea of producing bulk crystalline alloys composed of multiple components being added in proportions that are far beyond their binary solid solubility limits, yet yielding a single phase solid solution [3,4]. While in some cases the solid solutions formed possess simple crystal structures such as face-centered cubic (fcc) and body centered cubic (bcc) [5,6] and fulfill the expectations of combining high strength with good ductility [7], these successful cases constitute only a very small fraction of the significant efforts to experimentally obtain such single phase solid solutions. The underlying reason for such limited success is the very nature of the proposed alloy design strategy, which relies completely on the maximization of the configurational entropy [8–11]. The original HEA approach thus imposes the constraint of achieving this through equiatomic ratios of multiple alloying principal elements [1,12]. A limiting criterion of this type has failed to produce consistently the desired single phase solid solution forming compositions, resulting in the emergence of only a handful of equiatomic HEAs forming single phase solid solutions [3,13]. The most well-known of these is the equiatomic CoCrFeMnNi introduced by Cantor et al. [3,14–16] which forms a single fcc phase solid solution and exhibits excellent room temperature and cryogenic mechanical properties [17,18].

The present work aims at exploring the inherent flexibility involved in HEA design which would enable to overcome the limitations of HEA design concept. Following such an objective three distinct non-equiatomic single phase HEAs namely, $Fe_{40}Mn_{27}Ni_{26}Co_5Cr_2$, $Fe_{40}Mn_{40}Co_{10}Cr_{10}$ and $Fe_{37}Mn_{45}Co_9Cr_9$ (all in at%) were introduced by the authors recently [19–21], which exhibit exceptional stability and tensile properties. In all of these cases, even though the major constituents of the proposed non-equiatomic HEA are primarily the same as that of the alloy proposed by Cantor et al., the constituent proportions differ quite significantly, thus deviating from the existing HEA design

* Corresponding authors.
E-mail addresses: c.tasan@mpie.de (C.C. Tasan), d.raabe@mpie.de (D. Raabe).

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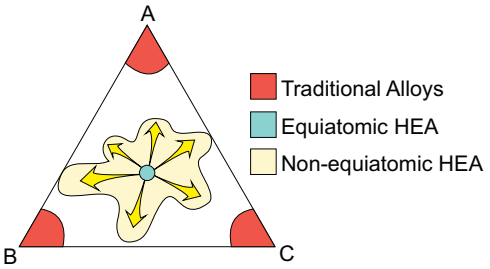

Fig. 1. A schematic comparison of traditional alloys with one base element and minor alloying additions, high entropy alloys with equiatomic compositions of all alloying elements, and non-equiatomic – yet still massively alloyed-high entropy alloys, on the isothermal cross section of a ternary phase diagram. The relaxation of the high entropy alloy criteria to include non-equiatomic compositions greatly expands the compositional ranges that can be probed and the associated accessible properties.

principles. In spite of the deviation, random single phase solid solution microstructures are successfully achieved. The recent investigation of Otto et al. demonstrated the weak dependence of single phase solid solution formability on configurational entropy [22]. Also, other works revealed that the configurational entropy curve of such materials assumes a rather flat shape so that a wide range of compositions outside of the equiatomic structure yield similar entropy values [19–21]. These results clearly show that alloy design approaches expanding towards non-equiatomic compositions have a great potential in opening up the applicability of HEAs for future applications as sketched in Fig. 1.

To demonstrate the significance of this concept, we i) introduce a series of such non-equiatomic high entropy alloys with varied chemical compositions; ii) demonstrate that a single phase solid solution is achieved in each of the introduced cases; iii) validate the stability of all those single phase solid solutions at elevated temperatures; and iv) investigate the mechanical properties in terms of bulk hardness and by tensile testing.

2. Experimental

In order to meet the above mentioned objectives, one of the previously introduced non-equiatomic alloys, namely, $Fe_{40}Mn_{27}Ni_{26}Co_5Cr_2$ (at%), is used as a starting material system. A detailed analysis by CALPHAD approach predicted that this multi-component system could retain the high temperature FCC phase upon quenching to room temperature [23]. Hence, compositional variations of the $Fe_{(64-x)}Mn_xNi_{27.7\pm1.3}Co_{5.6\pm0.3}Cr_{2.3\pm0.1}$ (at%) system with 5 different variants in $x=21$, 24, 27, 34, 38 are investigated and are designated as 21Mn, 24Mn, 27Mn, 34Mn and 38Mn alloys, as shown in Table 1 respectively. Note that various physical, thermodynamic and electronic parameters are also shown here, which will be discussed later in the discussion.

In order to understand the effect of alloy composition on the phase formation, microstructure evolution and the resulting mechanical properties of this system, an in-house developed combinatorial rapid alloy prototyping (RAP) methodology is employed [23,28]. This approach enables widely varying compositions to be metallurgically produced from a single master cast. The corresponding high purity raw metals (purity > 99.8%) were induction melted in a vacuum furnace maintained at an Argon atmosphere of 400 mbar pressure. In order to eliminate the typical cast-structures and to ensure microstructural homogeneity, hot-rolling was carried out on all as-cast blocks at 900 °C to 50% thickness reduction (from 10 mm to 5 mm) followed by homogenization at 1200 °C for 2 h in Ar atmosphere and water quenching. Microstructural characterization confirmed that the solidification structures were fully removed. Further grain refinement for mechanical property optimization was carried out through cold-rolling to 64% thickness reduction and subsequent annealing at 900 °C in Ar atmosphere for different holding times ranging from 5–120 min.

The preliminary phase formation and thermal stability characterization were carried out using X-ray diffraction (XRD) and differential scanning calorimetry (DSC). XRD measurements were carried out on a Huber-2 goniometer where the samples were exposed to Co Kα radiation ($\lambda=1.79$ Å). The Metero0D detector probed the 2θ range from 0° to 120° at a step size of $\Delta 2\theta=0.05°$. DSC experiments were performed in a SETARAM Setsys 16/18 device between 20 °C and 1300 °C at different rates (5–10 K min^{-1}) in Ar atmosphere. Microstructure characterization was carried out at all stages, i.e. on as-cast, hot rolled, homogenized, cold rolled and recrystallized samples. Emphasis is placed here on the homogenized, as cold rolled and subsequent annealed states. Secondary electron (SE) imaging, energy-dispersive X-ray spectroscopy (EDX) and electron backscatter diffraction (EBSD) were performed in a 6500F JEOL field emission gun-scanning electron microscope (FEG-SEM) equipped with an EDAX software and TSL OIM EBSD acquisition and analysis system. While the chemical homogeneity at micron-scale was investigated using EDX, the elemental distribution at the atomic scale across grain boundaries (GB) was studied using a local electrode atom probe (LEAP™ 3000X HR (Cameca Instruments)). Data analysis was performed using IVAS 3.6.8 software. Atom Probe Tomography (APT) specimens were target prepared from EBSD determined GBs using a FEI Helios Nanolab 600i dual-beam focused ion beam (FIB) following the procedures described in Ref. [29].

Mechanical properties of the homogenized, cold-rolled and recrystallized states were evaluated at room temperature on a Kammrath and Weiss GmbH tensile stage. Dog-bone-shaped specimens with gauge geometry of 4 mm × 2 mm × 1 mm were deformed at an initial strain rate of 2.5×10^{-3} s^{-1}. Prior to tensile deformation, one of the surfaces of the samples was metallographically polished for the deformation trace analysis, while a speckle pattern was applied to the opposite surface for strain measurement. The latter was carried out by digital image correlation (DIC) analysis (Aramis from GOM GmbH). In order to reveal the active deformation mechanisms, the microstructure of homogenized samples were investigated after the tensile tests. The imaging of the surface deformation features was carried out by employing the multi-focus imaging function of a Leica DM 4000M optical microscope (OM). The deformation induced

Table 1
Physical, thermodynamic and electronic parameters calculated for x-Mn alloys in comparison with the equiatomic composition.

x-Mn (at%)	Composition (at%)	δ [24] (%)	ΔH_{mix} [24] (kJ/mol)	ΔS_{conf} [25] (J/K · mol)	VEC [26]	e/a [27]	Ω [25]
21Mn	$Fe_{42.2}Mn_{20.7}Ni_{28.9}Co_{5.9}Cr_{2.3}$	4.16	−3.44	10.83	8.38	1.98	5.45
24Mn	$Fe_{41.1}Mn_{24.1}Ni_{27.1}Co_{5.5}Cr_{2.2}$	4.40	−3.52	10.89	8.31	1.98	5.32
27Mn	$Fe_{40.0}Mn_{27.0}Ni_{25.7}Co_{5.2}Cr_{2.1}$	4.58	−3.56	10.84	8.25	1.96	5.21
34Mn	$Fe_{29.4}Mn_{33.9}Ni_{28.5}Co_{5.8}Cr_{2.4}$	4.95	−4.40	11.13	8.24	2.00	4.70
38Mn	$Fe_{25.7}Mn_{37.6}Ni_{28.5}Co_{5.8}Cr_{2.4}$	4.92	−4.17	11.05	8.21	2.00	4.48
EA	$Fe_{20}Mn_{20}Ni_{20}Co_{20}Cr_{20}$	4.19	−4.16	13.38	8.00	1.80	5.76