University of Groningen

Size dependent plasticity and damage response in multiphase body centered cubic high entropy alloys

Basu, Indranil; Ocelik, Vaclav; De Hosson, J.T.M.

Published in:
Acta Materialia

DOI:
[10.1016/j.actamat.2018.03.015](https://doi.org/10.1016/j.actamat.2018.03.015)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2018

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Basu, I., Ocelik, V., & De Hosson, J. T. M. (2018). Size dependent plasticity and damage response in multiphase body centered cubic high entropy alloys. *Acta Materialia*, 150, 104-116.
<https://doi.org/10.1016/j.actamat.2018.03.015>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Full length article

Size dependent plasticity and damage response in multiphase body centered cubic high entropy alloys

Indranil Basu^{*}, Václav Ocelík, Jeff Th M. De Hosson

Department of Applied Physics, Zernike Institute for Advanced Materials and Materials Innovation Institute, University of Groningen, 9747AG, Groningen, The Netherlands

ARTICLE INFO

Article history:

Received 7 December 2017

Received in revised form

2 March 2018

Accepted 6 March 2018

Available online 10 March 2018

Keywords:

Nanoindentation

Electron back scatter diffraction

Spinodal decomposition

Serrated plastic flow

Order hardening

ABSTRACT

The paper concentrates on the prediction of damage behavior in BCC HEAs and its subsequent dependence on intrinsic length scales. Size dependent plastic response is investigated using correlative nanomechanical testing, high resolution microscopy and phase analysis. Hot forged multiphase $\text{Al}_{0.7}\text{CoCrFeNi}$ HEA, comprising both face centered cubic (FCC) and body centered cubic (BCC) structured phases were used. Phase characterization inside the BCC grains indicated spinodal decomposition leading to a periodic arrangement of ordered B2 and disordered A2 phases. Room temperature nano-indentation response in the BCC grain revealed appearance of repeated strain bursts occurring in a random and stochastic manner. The observed plastic behavior was correlated to dislocation hardening mechanisms arising from a combination of the spinodally modulated microstructure and order hardening effects. Interestingly, in contrast to the commonly observed FCC to BCC transformations, certain indents revealed a structural transition from BCC to FCC. The stress induced microstructural evolution is discussed in terms of inherent compositional gradients and relevant defect-interphase interactions.

© 2018 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The term “high entropy alloys”, also known as multi-principal element [1] or complex concentrated alloys [2,3], was introduced by Yeh et al. [4–7], based on the hypothesis that the high configurational entropy would stabilize the solid solution phase over competing intermetallic and elemental phases. They are ideally defined as a set of five or more elements, which are in equal, or near-equal, atomic ratios [2,8]. In the last decade, high entropy alloys (HEAs) have emerged as a new class of multicomponent metallic alloys providing the opportunity of exploring the vast compositional space in order to realize compositionally complex materials with a combination of several unique and unusual properties [2,9].

As per the original HEA design concept, phase separation was regarded as an undesired phenomenon as it suggested that the configurational entropy was insufficient for stabilizing a single solid solution state. Specific concerns regarding phase separation was the formation of potentially-embrittling intermetallic compounds or that the partitioning of alloying elements would abate

the expected solid solution hardening effect [6,10]. In this respect, several HEAs assuming a simple solid-solution structure, such as face-centered-cubic (FCC), body-centered-cubic (BCC), and/or hexagonal-close-packed (HCP) structures have been proposed [8,9,11–13]. However, a number of studies indicate that entropy stabilized single phase alloys are often hard to achieve and need not be endowed by superior properties, thereby digressing from the initially suggested phenomenon of the so called “cocktail effect” (one of the four core effects supposedly active in HEAs) observed in these class of alloys [3,10–15]. Formation of multiple phases in HEAs is primarily owing to precipitation or decomposition mechanisms arising from compositional fluctuations, local stress/strain heterogeneities, thermal-equilibrium behavior, and interatomic interactions among the constituent elements [9,11,16–21].

Depending on their crystal structure HEAs can display different mechanical properties. While the BCC-structured HEAs tend to exhibit high yield strengths and limited plasticity, the HEAs displaying an FCC structure are more ductile, highlighted by low yield strengths and easier plasticity [9,22]. In light of the aforementioned complications regarding manufacturing single-phase alloys, exploitation in the field of multiphase HEA fabrication has led to design of metastable multiphase alloy types that can overcome strength-ductility trade off effects [23–25]. For instance, by varying

^{*} Corresponding author.E-mail address: i.basu@rug.nl (I. Basu).

the content of Al in $\text{Al}_x\text{CoCrFeNi}$ HEAs, a mixture of FCC and BCC phases can be achieved that can theoretically possess the benefits of a ductile FCC phase along with the strength increment imparted by the BCC constituent phases [19,25,26]. However, considering the multiphase HEAs to be a conglomerate of different phases (comprising phase boundaries, precipitates, decomposed phases etc.), complex physical interactions between individual phases/elements during thermomechanical processing is an expected outcome.

In order to accurately assess the mechanical performance of multiphase HEAs and whether these class of alloys outperform the conventional structural materials, it is imperative to draw insights into the active physical mechanisms during deformation. In particular the individual response of different crystal structures and phases as well as the local strain compatibility effects across different interphases present in these alloys. While a large body of literature [3,6–8,15,27–29] is already dedicated to the microstructure control and design aspect of as-cast, homogenized and wrought processed HEAs, there is still a need of more thorough investigations probing into the subsequent effect of the microstructure and related strengthening behavior on the sub-micron/microscopic as well as macroscopic deformation response in these alloys. For instance, even though there are studies [22,30–32] reporting the deformation behavior of FCC HEAs to ensue through a combination of $\{111\}$ 110 planar slip and $\{111\}$ 112 mechanical twinning, the deformation behavior of BCC HEAs is still not well understood.

Another aspect influencing the deformation behavior in materials is their dependence on the length scale dynamics and associated defect topology. In this context, understanding the size effects on the mechanical response in HEAs is essential in order to categorize the role of various intrinsic length scales as determined by the dimensions of constituent phases on the generation and motion of crystal defects, such as dislocations, grain/phase boundaries etc. Unfortunately, only very few studies delve into the size effect associated deformation behavior in HEAs, especially at room temperatures [33–37]. Giwa et al. [33] performed micropillar compression on the individual FCC and BCC phase constituents in $\text{Al}_{0.7}\text{CoCrFeNi}$ HEAs. They reported that both FCC and BCC phases show a size dependent strengthening effect. Moreover, the BCC phases also revealed size dependent hardening behavior unlike the FCC phase. This was attributed to overall larger lattice resistance and Peierls barrier in the BCC HEAs. Nanoindentation investigations in refractory BCC HEAs [38] also corroborate the aforementioned phenomenon by reporting larger room temperature activation volumes for plastic deformation in comparison to conventional BCC alloys, resulting in relatively delayed plasticity in the former. However, a definitive correlation between the above mentioned small scale deformation response and the local microstructural strengthening effects in BCC HEAs is largely unknown.

The current work presents a detailed insight into small scale deformation response of BCC HEAs correlating the role of microstructure on local scale plasticity initiation and subsequent strain accommodation. Room temperature nanoindentation experiments are performed on the BCC phase in multiphase $\text{Al}_{0.7}\text{CoCrFeNi}$ HEA. The plastic flow is highlighted by an unusual appearance of multiple randomly occurring serrations. The observed plastic response and associated dislocation slip are discussed in light of spatial distribution of constituent phases and associated hardening effects. The observed trends serve as a significant advancement towards understanding damage behavior in BCC HEAs.

2. Experimental procedure

Multiphase high entropy alloys with nominal composition of

$\text{Al}_{0.7}\text{CoCrFeNi}$ were prepared by arc-melting, followed by homogenization at 1250 °C for 50hrs and upset forging at the same temperature resulting in a thickness reduction of 50% (as described in Ref. [19]). The final thickness of the forged buttons was ~ 5 mm. The resultant microstructure comprised of more than one phases possessing either FCC or BCC crystal structures [39].

Scanning electron microscopy (SEM) and electron back scattered diffraction (EBSD) technique were utilized for microstructural characterization. SEM and EBSD measurements were made using a Tescan Lyra dual beam (FEG-SEM/FIB) scanning electron microscope equipped with a Hikari Super CCD camera used for acquiring EBSD patterns. An accelerating voltage of 25 kV and current of 20 nA was used. A step size of 0.075 μm and hexagonal type of grid was used. A binning of 2×2 was used for collection of Kikuchi patterns using 640×480 CCD camera resolution. For localized high resolution EBSD mappings a step size of 0.05 μm and binning of 1×1 was implemented. The acquired raw EBSD data was subsequently analyzed using EDAX-TSL OIM™ Analysis 7 software and MTEX Matlab toolbox [40]. Noise reduction was performed with a threshold confidence interval of 0.2. The constituent phases were determined by energy dispersive spectroscopy (EDS) using an EDAX Octane Super EDS detector. In order to resolve the phase compositions inside the BCC grain, EDS measurements were performed with an accelerating voltage of 5 kV with the step width of 0.05 μm . However, it must be mentioned here that the limit of spatial and depth resolution of X-rays for the present conditions is realistically of the order of $\sim 0.15 \mu\text{m}$. EDS data collection and analysis was performed using EDAX Team 4.5 software. Phase fractions were determined from SEM images using ImageJ image analysis software.

Nanoindentation measurements were carried out employing an MTS Nano Indenter XP (MTS Nano Instruments, Oak Ridge, TN) with a cube-corner tip using the continuous stiffness measurement (CSM) technique. Load-controlled indentations were made inside the BCC grain to a maximum depth of 500 nm with a targeted strain rate of 0.05 s^{-1} , which corresponds to a maximum loading rate of the order of 0.1 mN/s. In order to calculate the strain rate sensitivity in BCC-HEA grain interior, additional indentation were made at different strain rates ranging from 10^{-2} to 10^{-4}s^{-1} . All measurements were corrected for indentation drift, wherein the experimental drift values were of the order of 10^{-3}nm/s . Values of hardness (H) and Young's modulus (E) were obtained from the load–displacement data for the indentations using the Oliver–Pharr method [41,42].

3. Results

3.1. EBSD analysis and nanoindentation response in BCC-HEA grain

A single BCC HEA grain was selected for performing indentation measurements. EBSD characterization were performed in and around the selected BCC-HEA grain to obtain information regarding the orientation and local strain induced due to the thermo-mechanical treatment described previously. Fig. 1 provides the EBSD analysis of one of the indented regions in the selected BCC-HEA grain. The mapping represents the microstructure prior to indentation. The mean grain orientations in IPF color coding are shown in Fig. 1a. The interphase boundaries between FCC and BCC grains are shown in white and the grain boundaries in black, described by a threshold misorientation of 3°. The BCC grain orientation can be described as $[001]$ parallel to the viewing axis i.e. surface normal. Nanoindentation tests were performed in different locations in the same BCC grain as illustrated by the schematic and inset SEM image showing three of such indents (c.f. Fig. 1a). Image quality map in Fig. 1b reveals strong contrast variation in the

Fig. 1. a) EBSD inverse pole figure (IPF) mapping of the investigated BCC HEA grain in $\text{Al}_{0.7}\text{CoCrFeNi}$ alloy. The orientation of the grain is described by the [001] direction along the viewing plane normal. A schematic of the indents (of depth 500 nm) made in the grain interior is additionally shown (similar indent profiles were also performed at other locations in the same grain to assess the overall mechanical response of the grain), inset SEM image corresponds to the same indent profile; b) IQ map indicating large strain induced contrast variations and substructure formation inside the BCC grain; c) Phase map separating the BCC (in green) and FCC (in red) grains in $\text{Al}_{0.7}\text{CoCrFeNi}$ HEA. BCC-FCC phase boundaries are highlighted in white and other grain boundaries (misorientation larger than 3°) shown in black. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

interior of the BCC grain, indicating large strain accumulation and sub-structure formation. Fig. 1c shows the phase map indicating islands of FCC grains surrounding the investigated BCC grain. The neighboring FCC grains show diverse orientations and are characterized by primarily a strain free interior (c.f. Fig. 1a and b).

Fig. 2 shows the load-depth curves corresponding to indentations performed in different areas of the same BCC-grain. All indents were made far away from the BCC-FCC interphase boundary (c.f. Fig. 1a) to avoid influence of the grain boundary on the indentation response. The loading curves show reasonably good reproducibility indicated by Fig. 2a. Fig. 2b display a magnified view of the initial loading response for 2 randomly selected indents from Fig. 2a, as a representation of the characteristic loading response of the indented BCC grain. The loading curve is highlighted by a typical elastic to plastic transition characterized by yield excursion

event of a magnitude in the range of $\sim 3\text{--}5\text{ nm}$. The initial elastic regime for both the indents in Fig. 2b agrees well with the Hertz elastic contact solution, wherein the load ' P ' varies linearly with $h^{1.5}$. Important to note is the small variations in the elastic to plastic pop in load and the corresponding indentation depth for different indents in the same grain. This effect, as will be discussed later, is directly correlated to the resultant strain accumulation in the BCC HEA grain due to the forging treatment. Loading in the elasto-plastic regime is highlighted by multiple non-periodic nanometer sized displacement bursts for all the indentation curves, highlighted by the black arrows in Fig. 2b. The serrated flow however dampens at increasing indentation depths with fewer occurrences of displacement bursts.

Fig. 2. a) Representative indentation load-displacement curves for four different indents made inside the BCC HEA grain; Highlighted region is magnified in b) showing the elastic to plastic transition and subsequent small scale pop in events in the plastic loading regime corresponding to 2 randomly selected indents, the elastic loading region shows excellent agreement with a Hertzian type loading with a spherical contact.

3.2. EDS phase composition and fraction analysis inside the BCC-HEA grain

Fig. 3 presents the EDS phase composition and fraction analysis performed both inside the BCC-HEA Grain 1 as well as across the BCC-FCC interphase. Fig. 3a shows the spatial distribution of Al, Co, Cr, Fe and Ni inside the FCC and BCC grains. The BCC grain indicates presence of two phases represented by different SEM image contrast i.e. bright and dark regions. The phases exhibit an elongated morphology and are arranged in a weave like pattern. The bright phase shows a higher concentration of Cr atoms, whereas the darker ones are rich in Al and Ni. These are known to be the disordered A2 phase and ordered B2 phase [21,43–45], as highlighted in Fig. 3a, both of which crystallize in BCC structure. The Co and Fe atoms tend to show a weak preference towards segregation

in the A2 phases. The respective phase area fractions measured were $\sim 50\%$ ($\pm 2.6\%$), with particle sizes for the A2 phase ranging from 20 to 810 nm and a mean particle width of ~ 121 nm (standard error (SE) = 0.46) (c.f. Fig. 3b).

3.3. Indentation induced phase transformation in BCC-HEA grain

EBSD phase analysis of the microstructure in the vicinity of few of the indents made in the BCC-HEA grain interior showed instances of newly formed FCC grains post indentation (c.f. Fig. 4a and b). Compared to the mappings acquired prior to indentation, the same region showed no traces of FCC grains (see inset image in Fig. 4a), thus indicating such phase transformation must have occurred during indentation. Out of the 9 indents made in the BCC grain in Fig. 4a, 4 of them showed clear evidence of phase change

Fig. 3. a) EDS elemental maps showing spatial distribution of Cr, Fe, Co, Ni and Al and corresponding SEM image of investigated area. White regions correspond to disordered A2 phase and dark grey ones represent the ordered B2 phase; b) A2 phase size distribution analysis.

Fig. 4. a) IPF map showing indents made in the BCC grain, with few of them indicating indentation induced BCC to FCC phase transformation. Inset image showing the same region prior to indentation with no traces of FCC grains. BCC-FCC phase boundaries are highlighted in white and other grain boundaries (misorientation larger than 3°) shown in black; b) Magnified IPF + IQ map of the vicinity of Indent A, corresponding SEM and Forward scatter detector images showing distribution of A2 and B2 phases. BCC-FCC Phase boundaries are overlaid with Kurdjumov-Sachs orientation relationship shown in red, with an angular deviation of $\pm 5^\circ$; c) Indentation load-displacement curves for indents with and without BCC-FCC phase transformation; d) Point to point misorientation profile across newly formed BCC-FCC phase boundaries, from point I to II. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

from BCC to FCC in the indent vicinity. When the IPF maps near the indents are compared with the SEM and forward scatter detector (FSD) images of the same region, it is revealed that these FCC grains seem to arise from the disordered A2 parent BCC phase (c.f. Fig. 4b).

Comparing the indentation flow curves corresponding to an indent with phase transformation (marked as A in Fig. 4a and c) and one without (marked as B in Fig. 4a and c) indicates appearance of distinct displacement burst events during the initial segment of the load-displacement curve for indent A (see pop-in events highlighted by double-sided arrows in Fig. 4c), which are absent in the indentation response of indent B. Misorientation analysis across the newly formed phase boundary during indentation, indicates an orientation relationship between the parent BCC grain and FCC phase lying close to the Kurdjumov-Sachs (K-S) relationship defined by the $\{111\}_{\text{FCC}} \parallel \{110\}_{\text{BCC}}$ and $\langle 110 \rangle_{\text{FCC}} \parallel \langle 111 \rangle_{\text{BCC}}$ (see phase boundaries in red in Fig. 4b and misorientation profile in Fig. 4d). An angular deviation of $\pm 5^\circ$ was considered.

4. Discussion

The present work investigates the plasticity behavior associated with BCC phases in multiphase $\text{Al}_{0.7}\text{CoCrFeNi}$ HEAs at material intrinsic length scales. By means of correlative nanoindentation

and EBSD/EDS analysis, a correlation between local mechanical response and microstructure in BCC grain interior is established. The results indicated interesting size effects on the plastic response in the grain interior, which are not expected in typical room temperature deformation response. The current section discusses in detail the underlying mechanisms active during small scale plastic deformation inside the BCC-HEA grain and associated influence of dimensional constraints imposed by the local microstructure. In particular the role of interphase boundary inside the BCC grain is discussed in terms of deformation response.

4.1. Initiation of plasticity in BCC-HEA grain interior

The onset of plasticity typically corresponds to the first observed yield excursion, which under a load-controlled indentation manifests as displacement burst at a nearly constant load. Due to the extremely small sized volumes probed during nanoindentation, plastic yielding either corresponds to homogeneous nucleation of dislocations or by means of heterogeneous activation of pre-existing dislocation sources underneath the indenter tip. The mode of plasticity initiation is determined by the relative difference between indented volume ($\propto R^3$, where R is the radius of the indentation volume) during plastic yielding and the mean

dislocation spacing ' $d_{\perp}'$ in the region. In the case of ' R ' being smaller than ' $d_{\perp}'$, plastic yielding will occur via homogenous nucleation of dislocations, whereas in the opposite scenario plasticity is suggested to be triggered by mobilization and/or multiplication of already present dislocation sources [46–49]. In principal the former will be expected to exhibit yielding at stresses close to the 'theoretical shear strength' of the material.

The BCC grain in the $\text{Al}_{0.7}\text{CoCrFeNi}$ HEA carried significant plastic strain prior to indentation (c.f. Fig. 1b), whereby the initial mean dislocation density (measured from local misorientation data) in the grain interior was of the order of $\rho_{\text{GND}} \sim 10^{15} \text{ m}^{-2}$. Considering the dislocation spacing ' $d_{\perp}'$ to be defined as $1/\sqrt{\rho_{\text{GND}}}$, an average dislocation spacing of $\sim 30 \text{ nm}$ is obtained. Using the Hertzian contact theory between a spherical tip and substrate in the elastic regime, an estimate of the effective spherical contact radius ' R_{eff} ' at the onset of plasticity in the BCC-HEA grain can be determined by the following expression [50],

$$P = \frac{4}{3}E^* \sqrt{R_{\text{eff}}h^3} \quad (4.1)$$

where P is the applied load at yield excursion defining the transition from elastic to plastic behavior, h is the instantaneous indentation depth at the onset of the pop-in event, and E^* is the reduced elastic modulus given by: $E^* = [(1 - \nu_s^2/E_s) + (1 - \nu_i^2/E_i)]^{-1}$. In the reduced elastic modulus equation, $\nu_i = 0.07$ and $E_i = 1141 \text{ GPa}$ are the Poisson's ratio and Young's modulus of the diamond indenter, respectively; $\nu_s = 0.25$ and $E_s = 275 \text{ GPa}$ are the Poisson's ratio and the 'indentation' Young's modulus in the BCC-HEA grain, respectively. An empirical fit of the load-displacement curve in the elastic regime for indentation in the BCC grain interior (c.f. Fig. 2b) as per Eqn. (4.1) gives an estimate of the value of R to be in the range of $160 \pm 10 \text{ nm}$, which is approximately an order of magnitude larger than the mean dislocation spacing ' $d_{\perp}'$. This alludes to a case where pre-existing dislocations beneath the indenter primarily contribute to plastic yielding.

The suggested mechanism can be additionally validated by determining the shear stress corresponding to the applied load at the first pop in event. The resolved shear stress (τ_{RSS}) to initiate dislocation slip during indentation can be expressed as [50,51],

$$\tau_{\text{RSS}} = \left(\frac{0.47}{\pi}\right) \left(\frac{4E^*}{3R}\right)^{2/3} P^{1/3} \quad (4.2)$$

where P is the applied load corresponding to the first pop-in in the bulk. Due to the spatial heterogeneity in the stored dislocation densities (c.f. Fig. 1b) in the hot forged alloy (c.f. Fig. 5) the pop-in loads corresponding to multiple indentations performed in different parts of the same BCC HEA grain showed a large spread ranging from 0.045 to 0.1 mN. Substituting the experimentally measured pop-in load values into Eqn. (4.2) the resolved shear stress in the grain interior is obtained in the order of $\sim G/20$ (5.6 GPa) to $G/24$ (4.7 GPa), where $G = E_s/2(1 + \nu)$ is the shear modulus in GPa. Comparing these values to the theoretical shear strength, typically ranging between $\sim G/5 - G/15$, indicates plastic deformation in the present case occurs at much lower stresses than those needed to nucleate dislocations.

4.2. Hardening mechanisms and serrated plastic flow during nanoindentation in the BCC-HEA grain

During plastic loading, indentation flow curves in the BCC-HEA grain continue to exhibit abrupt displacement bursts of varying magnitudes appearing at random intervals. Appearance of discrete strain bursts in the plastic regime physically demonstrate a phenomenon wherein dislocation motion occurs under significant intrinsic resistance [52]. Apart from the conventionally observed dynamic strain aging phenomenon due to solute impurity-dislocation interactions, serrations could also arise from local starvation of dislocation sources, mutual interference of dislocation stress fields or presence of obstacles that retard dislocation motion, such as statistically entangled dislocation configurations and presence of interfaces (shearing of precipitates, grain boundaries etc.) [53–55]. In all the above cases the motion of dislocations is characterized as jerky, highlighted by intermittent periods of rapid glide that manifest as displacement bursts in the loading curve.

Fig. 6a shows the distribution of displacement burst sizes Δh with indentation depth in BCC-HEA grain 1. The statistics indicate a highly stochastic behavior revealing no definitive trend. The recorded burst sizes range from 2 nm to 22 nm. The plot clearly indicates a concentration of discrete bursts at lower indentations depths that with increasing loads seem to significantly reduce in frequency and are more or less abated for depths larger than 400 nm. If it is assumed that each displacement burst physically signifies a particular strain accommodation event then the characteristic quantity, $\epsilon^P = \ln \left(\frac{h + \Delta h}{h} \right)$ (where h is the instantaneous indentation depth) gives the measure of the accommodated plastic shear strain. Fig. 6b shows the variation of plastic strain corresponding to each burst event as a function of the instantaneous indentation depth, wherein strain values can vary from 0.8% to 20%. Assuming a singular displacement burst event is associated with glide of a set of dislocations, each inducing an individual shear of magnitude equal to the dislocation burgers vector b , the displacement burst size Δh can be then roughly correlated to the number of activated dislocations n for a singular event by the following expression [51],

$$\Delta h = n \cdot b \quad (4.3)$$

Concurrently the local plastic shear strain γ^P produced by such dislocation motion for each pop-in can be equated to the accommodated true strain ϵ^P . The local plastic shear γ^P can be further expressed as the sum total of individual shears borne by each dislocation segment, using the Orowan equation,

Fig. 5. Experimentally measured first (elastic to plastic transition) pop-in loads for different indents made in the same BCC-HEA grain.

Fig. 6. a) Variation of displacement burst sizes with the corresponding instantaneous indentation depth; b) Variation of strain accommodated for each burst event with respect to the instantaneous indentation depth.

$$\ln \left[\frac{(h + \Delta h)}{h} \right] = \gamma^p = \frac{n \cdot b}{L} \quad (4.4)$$

where L is the mean slip distance a set of n dislocations need to traverse to accommodate strain from one displacement burst. Combining Eqns (4.3) and (4.4) an estimate of L is achieved in the range of ~25–620 nm. Statistical analysis of the displacement and strain bursts, provides a mean burst size of 5 nm and strain value of 4%. The corresponding mean value of L for all the observed pop-in events can be then calculated as 125 nm.

In the present alloy, the indented body-centered cubic HEA grain comprises of a Ni- and Al-rich ordered BCC phase (denoted as B2 in Fig. 3a) interspersed with a disordered Fe- and Cr-rich BCC phase (highlighted as A2 phase in Fig. 3a). These phases are known to form during the solidification process, wherein the interdendritic regions solidify first as a disordered A2 phase and on further cooling undergo spinodal decomposition to generate a modulated microstructure with periodically arranged B2 and A2 phases in a weave like morphology [21]. The heat treatment during homogenization and hot forging further drives preferential segregation of Ni and Al atoms in B2 phase, whereas the Fe and Cr elements form alternating Fe-rich and Cr-rich regions in the disordered A2 phase. It is well known that the tendency of formation and stability of spinodal microstructures in the BCC grain is promoted by the increasing content of Al in the HEAs [21,26,45]. The observed stability of the spinodal microstructure, even after long duration heat treatment at high temperatures, is attributed to the relatively high Al content in the investigated HEA [29,45]. Interestingly the mean A2 particle size values shown in Fig. 3b are reasonably close to the calculated mean dislocation glide length corresponding to each strain burst observed during indentations in the bulk BCC grain.

In light of the aforementioned observations, it is suggested that the observed staircase flow behavior is triggered by the resistance generated by interfacial strengthening mechanisms between the elastically stiffer B2 matrix and soft A2 phase, against the dislocation motion. Fig. 7a gives a simplified illustration of the deformation behavior beneath the indenter tip. The BCC-HEA grain exhibits a composite like microstructure wherein the white A2 phases act as the plastically weaker zones compared to ordered B2 phase shown in dark grey. As the indenter penetrates into the BCC grain (direction indicated by the blue arrow in Fig. 7a), it is expected that dislocation activation and plastic deformation initiates primarily in

the A2 phases (lying underneath the indenter tip), whereby dislocation glide can occur easily, manifesting as displacement bursts in the indentation loading curve. These dislocations are depicted in green with the forward stress component along the glide direction shown by the green arrow (c.f. Fig. 7a). As the first set of mobilized dislocation reach the A2-B2 interphase boundary, they experience a back stress generated from the interfacial hardening (illustrated by the retarded red dislocations with direction of back stress shown by red arrow). Subsequently the load starts to increase rapidly until local stresses become large enough to activate new dislocation sources inside one or many of the A2 lamellae lying within the plastically affected zone around the indenter, highlighted by the dashed contours. The contour colors, in Fig. 7a, transition from yellow to blue schematically indicating progressively decreasing applied strain values on moving away from the indenter tip. These new dislocations will glide freely inside the A2 phases until they are again stopped at the interphase boundary. This process repeats as the plastic deformation zone around the indenter becomes larger and larger with increasing penetration depth, giving rise to a staircase type yielding. As the applied load increases more and more, it is likely that the local stresses become high enough in certain regions to overcome the strengthening stress barrier such that dislocations can now traverse through both the disordered and ordered phases. This explains the observed dampening of serration events at higher indentation loads or greater depths (c.f. Fig. 6). The proposed deformation mechanism is experimentally validated by the observations of high local strain zones present along the interphase inside the BCC-HEA grain (c.f. Fig. 7b and c). Fig. 7b and c also indicate that strain borne by the relatively softer A2 phase is considerably higher than the ordered B2 matrix, owing to a relatively resistance free dislocation motion in the former and subsequently greater dislocation activity. Cumulative misorientation profile (with respect to point I in Fig. 7d) and kernel average misorientation (KAM) gradients (c.f. Fig. 7d) inside the B2 phase indicate a clear concentration of strain near the interface (KAM values of 0.7°) and a nearly strain free interior in the B2 phase (evinced by KAM values between 0.1° and 0.2°). The misorientation between the interphase and phase interior are of the order of 0.4° .

The observed dislocation strengthening in the BCC grain is attributed to combined effect of a spinodally modulated microstructure and order hardening effects. In principal the former contribution induces hardening prior to dislocation shearing (at the

Fig. 7. a) Schematic illustrating plastic deformation in the BCC-HEA grain interior during indentation. White regions correspond to A2 phases and dark grey areas describe the ordered B2 phases. The strain field due to the indenter is schematically shown by dashed contour lines moving from yellow near the indenter (high strains) to blue far away from the indenter (low strains). Green arrows indicate the direction of applied shear from indentation that move dislocations in the plastic zone around the indenter. Red arrows indicate the back stresses from spinodal and order hardening effects imposed on the dislocations, thereby blocking them at the A2-B2 interphase. h is the instantaneous indentation depth; b) Kernel Average misorientation (KAM) map inside the BCC-HEA grain with threshold misorientation of 2° and using first nearest neighbor indicating strain accumulation in the A2

A2-B2 interphase boundary), and the latter leads to hardening during the shearing process of the ordered B2 phase. Typically the larger of the two accounts for the overall hardening experienced during plastic deformation. The forthcoming paragraphs discuss in detail the individual contributions of these mechanisms.

Spinodal microstructures typically arise due to instability with respect to a nonlocal compositional perturbation that is small in degree (in comparison to concentration gradients for nucleation and growth induced precipitation) but large in extent. Unlike in conventional precipitation hardening mechanisms, the changes in lattice misfit and shear modulus inducing parastic and dielastic strengthening, respectively, are much more gradual and periodic. Thereby the effects of the increment on the local yielding strongly depends upon amplitude of compositional fluctuation Δ and the feature size of the spinodal structure, denoted as the wavelength λ [56–58]. By contrast to FCC spinodal alloys, wherein hardening is primarily due to coherency strains, the compositional fluctuations in BCC spinodal alloys can be significantly larger such that an additional effect of modulus difference on hardening cannot be neglected [59].

Kato formulated the respective contributions of lattice misfit or coherency hardening and modulus hardening for BCC spinodal microstructures [59]. By assuming a co-sinusoidal modulation in the composition and an elastically isotropic material, the degree of hardening due to lattice misfit effect ' $\Delta\sigma_\epsilon$ ' can be expressed as,

$$\Delta\sigma_\epsilon = \frac{0.5\Delta\eta E}{1-\nu} \quad (4.5)$$

In the above expression, η corresponds to the variation in lattice constant and is defined as [56–58],

$$\eta = \frac{d(\ln a)}{dC} = \frac{\delta a}{a \cdot dC} \quad (4.6)$$

where a is the lattice constant and $\frac{\delta a}{dC}$ is the ratio of variation in lattice parameter between the A2 and B2 phases over the relative change in atomic concentration. A secondary hardening contribution ' $\Delta\sigma_G$ ' manifests from the difference in shear modulus given as,

$$\Delta\sigma_G = \frac{0.65\Delta Gb}{\lambda} \quad (4.7)$$

where ΔG is the difference in shear moduli of the disordered A2 and ordered B2 phases, b is the dislocation burgers vector. The resultant hardening from spinodal decomposition ' $\Delta\sigma_{spinodal}$ ' is therefore expressed as,

$$\Delta\sigma_{spinodal} = \Delta\sigma_\epsilon + \Delta\sigma_G \quad (4.8)$$

In the HEA studied here, the lattice mismatch between the B2 and A2 phase is of the order of 0.5% and primarily depends upon the composition of Al [60]. EDS analysis was used to obtain the compositional fluctuation of Al between the A2 and B2 phases as well as across the BCC-FCC interphase (c.f. Fig. 8a). The compositional fluctuation of Al across the BCC grain showed a variation between a minimum value of 6% in the A2 phase to a maximum of 25% in ordered B2 lamella. Subsequently the amplitude Δ for Al is calculated as ~9.5% (c.f. Fig. 8b). Fig. 8b can also be used to obtain the mean wavelength, defined by the total distance divided by the number of Al compositional peaks, giving a value of ~117 nm. This is reasonably close to the measured mean spinodal feature size of

121 nm. With respect to the difference in shear modulus, the single crystal shear modulus ' $G_{B2<100>}$ ' for B2-NiAl crystal oriented along $\langle 100 \rangle$ (since the indented grain orientation is close to $\langle 100 \rangle$) is obtained directly from the value of $c_{44} \sim 114$ [61–63]. Using the shear modulus ' $G_{indentation}$ ' derived from indentation modulus, E_s and Poisson ratio, ν_s and applying the rule of mixtures, we get

$$G_{A2<100>} = \frac{G_{indentation} - [(1-f^{A2})G_{B2<100>}]}{f^{A2}} = 94 \text{ GPa} \quad (4.9)$$

Subsequently ΔG is estimated in the order of 20 GPa. It must be noted here that in order to simplify the analysis, precipitates shape effects is not considered in all of the above expressions. Substituting the above values in Eqns. (4.6)–(4.8), gives an approximate measure of spinodal strengthening $\Delta\sigma_{spinodal} \sim 514$ MPa ($\Delta\sigma_\epsilon = 486$ MPa and $\Delta\sigma_G = 28$ MPa). The values calculated indicate the spinodal hardening effects at the A2-B2 interphase inside the BCC grain can be substantial.

Apart from spinodal hardening, the creation of antiphase domains due to dislocation motion inside the ordered B2 phase should result in additional lattice resistance against easy glide. An approximate measure of the degree of order hardening in the present alloy can be given as [58,64,65],

$$\Delta\sigma_{ordering} = 0.8 \cdot \frac{\gamma_{APB}}{2b} \left[\left(\frac{3\pi f}{8} \right)^{0.5} - f \right] \quad (4.10)$$

where γ_{APB} is the antiphase boundary energy of B2-NiAl, with values estimated 0.8 J/m^2 [58], f is the volume fraction. Substituting the required values in Eqn (4.10) gives the degree of $\Delta\sigma_{ordering}$ in the range of ~340 MPa. Comparing the hardening contributions from ordering effects and spinodal decomposition, it can be deduced that the dislocations experience the maximum resistance at the interphase boundary i.e. hardening due to misfit and modulus difference arising from the spinodal decomposition.

A direct measure of the degree of resistance to slip motion in metals is the mean volume of atoms required to activate dislocation motion, also referred to as activation volume. Theoretically, greater the resistance to dislocation motion, higher the activation volume associated with initiation of plasticity. In the current work, activation volume V^* in the BCC-HEA grain is calculated as [38],

$$V^* = \frac{kT}{m\tau_{RSS}} \quad (4.11)$$

where m is the strain rate sensitivity experimentally measured by plotting the variation of resolved shear stress for plasticity initiation in the BCC grain to the applied strain rate, given by the relationship $\tau \propto \dot{\epsilon}^m$ (c.f. Fig. 9); k and T are the Boltzmann constant (J/K) and temperature (K), respectively. Substituting the resolved shear stress values corresponding to the strain rate of 0.01 s^{-1} in Eqn. (4.11), indicate an activation volume in the range of $\sim 5\Omega$, where Ω is equal to one atomic volume (b^3). This is nearly 5–10 times larger than activation volumes for pure metals at room temperatures that are in the range of $0.5\text{--}1 \Omega$ [38,66–69], indicating that activating dislocation motion is relatively difficult in BCC-HEA grain owing to the previously described hardening effects.

It must be noted that a positive strain rate sensitivity determined in the present case precludes dynamic strain aging (DSA)

Fig. 8. a) High resolution EDS line scan to configure compositional profile along A2 and B2 lamella and across the BCC-FCC phase boundary; b) Compositional fluctuations of Al and Cr along the probed distance, shown in atomic percent. Both Al and Cr reveal modulated wave-like concentration profile, with their values being in antiphase to each other. Compositional peaks of Al are further indicated by green arrows. Encircled areas show that the fluctuations can lead to the local Al content being quite similar in the BCC and FCC grains. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 9. Logarithmic plot of resolved shear stress with respect to different applied strain rates. The slope of the curve is used to determine the strain rate sensitivity m .

Fig. 10. SEM image of a cube corner indent made up to a depth of 2 μm inside the BCC-HEA grain, without any traces of crack nucleation.

effects in correlation with observed serrations. However, the aforementioned mechanism of dislocation pile-up at A2-B2 interface due to spinodal hardening effects and preferential glide in A2-BCC phases that give rise to stick-slip dislocation dynamics need not necessarily be associated with negative strain rate sensitivity (as in the case of DSA mechanism). On the other hand, considering that the length scale of deformation during nanoindentation is comparable to the scale of stress fluctuations resulting from the aforementioned phenomenon, it is quite likely that these physical mechanisms may manifest as serrations in the indentation load-displacement curve. In fact, it has been shown previously that dislocations shearing coherent precipitates can lead to serrated flow behavior despite a positive strain rate sensitivity value [55,70–72]. It must be further noted that unlike DSA phenomenon where serrations would typically continue till the end of the loading, the strain bursts in the present study dampen at increased loads and larger indentation depths transitioning into a smooth flow behavior.

The aforementioned values directly corroborate the high strengths and difficult plasticity behavior exhibited by BCC HEAs, which correlates to their abated macroscale damage resistance. Also noteworthy is the influence of size dependent deformation in ductility enhancement of BCC HEAs, wherein despite the high locally induced strains (approx. 20–28%) by the cube corner indenter, material fracture was not observed even for large indentation depths (up to 2 μm) (c.f. Fig. 10).

4.3. Nano indentation induced local BCC to FCC phase transformation

The results in the current work show evidence of indentation induced phase transformation of BCC-A2 phase to FCC phase in HEAs. Considering that all indentations were performed at room temperature, a thermal origin of the observed phase transformation is not feasible. This leaves the only possible pathway, wherein the BCC crystal structure is transformed into FCC via displacive mechanisms. The fact that the orientation relationship between the parent BCC grain and newly formed FCC phase agrees with a K-S type relationship (c.f. Fig. 4b and d), further indicates that the transformation is of martensitic origin i.e. shear induced. Such local structural transformation can be triggered by local elastic distortions generated owing to fluctuations in chemical composition and stress concentration.

The indentation flow curves corresponding to the indents associated with phase transformation showed additional pop-in events recorded during the initial loading regime. The corresponding resolved shear stress at onset of the highlighted burst events for indent A (c.f. see double sided arrows in Fig. 4c), as calculated from Eqn. (4.2), yield values of 4.3 GPa and 4.6 GPa respectively. In comparison the local resolved shear stress value at the onset of plastic deformation can be calculated from the load-displacement curve for the indent not showing a phase transformation (c.f. Indent B in Fig. 4c) as 5.6 GPa, which shows excellent corroboration with values obtained in section 4.1.1. Interestingly, the stress values associated with the highlighted pop-ins seen only for the indentation leading to phase transformation (c.f. Fig. 4c) are smaller than the critical resolved shear stress for plastic deformation, thereby suggesting activation of elastic strain accommodation mechanisms by means of local volume change in the vicinity of these indents. Furthermore, the excellent Hertzian dependence of the loading curve even after the two displacement bursts (c.f. Fig. 4c) suggests that indentation response during the pop-in events was still in the elastic loading regime. Infact, the beginning of plastic flow for the indentation in region A occurs at a later stage as marked by black arrows in Fig. 4c. These observations

directly correlate with the concurrent microstructural evidence of indentation induced local crystallographic phase transition from BCC to FCC (c.f. Fig. 4a and b), which is also associated with a net volume change.

The stability and formation of BCC structures in $\text{Al}_{0.7}\text{CoCrFeNi}$ HEAs is chemically determined by the atomic fraction of Al, such that with increasing Al content structural transformation from FCC to BCC is favored. Previous studies [73,74] have shown such tendency of the disordered BCC phase in $\text{Al}_{0.7}\text{CoCrFeNi}$ HEA to transform into FCC during high temperature compression experiments. In the current HEA, the BCC grain comprised of an Al-rich B2 phase and an Al-deficient disordered A2 phase. EDS compositional analysis indicated that the local Al concentration in certain regions of A2 phase can drop down to values similar to the composition measured in the FCC grain (see encircled segments of the composition profile in Fig. 8b). This is owing to the long duration homogenization treatment as well as hot forging, wherein the induced strain and thermal energy lead to significant segregation of Al and Ni atoms in the B2 phase and simultaneously created regions depleted in Al. The local decrease in Al content directly affects the stability of the BCC phase, making these regions prone to structural changes that may facilitate reversion into a more stable FCC phase. In the present study the applied stress during indentation most likely acts as a trigger to initiate the transformation of these metastable BCC A2 phases into FCC. Considering that the A2 phase is enriched with Cr, which is known to stabilize the BCC structure, explains the non-ubiquity of the observed phase transformation. It is possible that the probability of stress-induced transformation is dependent upon the local stored strain and compositional fluctuations of Al and Cr. The current results raise important questions on the stoichiometry associated stability of BCC phases in $\text{Al}_{0.7}\text{CoCrFeNi}$ HEAs at room temperature. Further work regarding exact quantification of the critical parameters triggering such transformation as well as the role of chemistry and local stresses on such events is underway.

5. Conclusions

Nano indentation induced microplasticity inside the BCC phases in $\text{Al}_{0.7}\text{CoCrFeNi}$ HEAs is investigated in order to assess the influence of local microstructure on small scale plastic response. The results highlight the role of defects during indentation strain accommodation and also their subsequent contribution to damage response. The following key conclusions were derived:

1. Onset of nanoscale plasticity inside the BCC grain in $\text{Al}_{0.7}\text{CoCrFeNi}$ HEA occurs by heterogeneous activation of pre-existing dislocation sources underneath the indenter tip.
2. Plastic deformation in the BCC-HEA grain interior is characterized by multiple displacement bursts occurring in a random manner. The bursts are correlated to the local interphase hardening behavior due to the spinodally decomposed microstructure, whereby the deformation is concentrated in the disordered A2 phase islands. The B2 phase additionally hardens by means of order hardening mechanisms that further makes dislocation motion in this phase difficult.
3. At higher indentation depths the observed serrations dampen, owing to applied stresses being high enough in order to overcome the strengthening stress barrier and initiated plasticity homogeneously in both the A2 and B2 phases
4. Certain indents in the BCC grain interior showed shear induced phase transformation to FCC crystal structure, owing to local compositional fluctuations and high stress concentrations.

Acknowledgments

This research was carried out under project number T61.14545 in the framework of the Research Program of the Materials innovation institute (M2i) (<http://www.m2i.nl/>). The authors also acknowledge P.K. Liaw for providing material for the study.

References

- [1] M.C. Gao, J.-W. Yeh, P.K. Liaw, Y. Zhang, *High-entropy Alloys: Fundamentals and Applications*, Springer, 2016.
- [2] D.B. Miracle, O.N. Senkov, A critical review of high entropy alloys and related concepts, *Acta Mater.* 122 (2017) 448–511, <https://doi.org/10.1016/j.actamat.2016.08.081>.
- [3] C. Woodward, D.B. Miracle, J.D. Miller, O.N. Senkov, Accelerated exploration of multi-principal element alloys with solid solution phases, *Nat. Commun.* 6 (2015) 6529, <https://doi.org/10.1038/ncomms7529>.
- [4] 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, *Adv. Eng. Mater.* 6 (2004) 299–303, <https://doi.org/10.1002/adem.200300567>.
- [5] J.-W. Yeh, Physical metallurgy of high-entropy alloys, *JOM* 67 (2015) 2254–2261, <https://doi.org/10.1007/s11837-015-1583-5>.
- [6] J.-W. Yeh, S.-J. Lin, T.-S. Chin, J.-Y. Gan, S.-K. Chen, T.-T. Shun, C.-H. Tsau, S.-Y. Chou, Formation of simple crystal structures in Cu-Co-Ni-Cr-Al-Fe-Ti-V alloys with multiprincipal metallic elements, *Metall. Mater. Trans.* 35 (2004) 2533–2536, <https://doi.org/10.1007/s11661-006-0234-4>.
- [7] J.-W. Yeh, Alloy design strategies and future trends in high-entropy alloys, *JOM* 65 (2013) 1759–1771, <https://doi.org/10.1007/s11837-013-0761-6>.
- [8] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent, Microstructural development in equiatomic multicomponent alloys, *Mater. Sci. Eng., A* 375–377 (2004) 213–218, <https://doi.org/10.1016/j.msea.2003.10.257>.
- [9] Y. Zhang, T.T. Zuo, Z. Tang, M.C. Gao, K.A. Dahmen, P.K. Liaw, Z.P. Lu, Microstructures and properties of high-entropy alloys, *Prog. Mater. Sci.* 61 (2014) 1–93, <https://doi.org/10.1016/j.pmatsci.2013.10.001>.
- [10] K.G. Pradeep, N. Wanderka, P. Choi, J. Banhart, B.S. Murty, D. Raabe, Atomic-scale compositional characterization of a nanocrystalline AlCrCuFeNiZn high-entropy alloy using atom probe tomography, *Acta Mater.* 61 (2013) 4696–4706, <https://doi.org/10.1016/j.actamat.2013.04.059>.
- [11] F. Otto, A. Dlouhý, 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 Mater.* 112 (2016) 40–52, <https://doi.org/10.1016/j.actamat.2016.04.005>.
- [12] F. Otto, Y. Yang, H. Bei, E.P. George, Relative effects of enthalpy and entropy on the phase stability of equiatomic high-entropy alloys, *Acta Mater.* 61 (2013) 2628–2638, <https://doi.org/10.1016/j.actamat.2013.01.042>.
- [13] S. Praveen, B.S. Murty, R.S. Kottada, Alloying behavior in multi-component AlCoCrCuFe and NiCoCrCuFe high entropy alloys, *Mater. Sci. Eng., A* 534 (2012) 83–89, <https://doi.org/10.1016/j.msea.2011.11.044>.
- [14] 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 Mater.* 100 (2015) 90–97, <https://doi.org/10.1016/j.actamat.2015.08.050>.
- [15] O.N. Senkov, J.D. Miller, D.B. Miracle, C. Woodward, Accelerated exploration of multi-principal element alloys for structural applications, *Calphad* 50 (2015) 32–48, <https://doi.org/10.1016/j.calphad.2015.04.009>.
- [16] N.G. Jones, K.A. Christofidou, H.J. Stone, Rapid precipitation in an Al0.5CrFeCoNiCu high entropy alloy, *Mater. Sci. Technol.* 31 (2015) 1171–1177, <https://doi.org/10.1179/1743284715Y.0000000004>.
- [17] E.J. Pickering, H.J. Stone, N.G. Jones, Fine-scale precipitation in the high-entropy alloy Al0.5CrFeCoNiCu, *Mater. Sci. Eng., A* 645 (2015) 65–71, <https://doi.org/10.1016/j.msea.2015.08.010>.
- [18] E.J. Pickering, R. Muñoz-Moreno, H.J. Stone, N.G. Jones, Precipitation in the equiatomic high-entropy alloy CrMnFeCoNi, *Scripta Mater.* 113 (2016) 106–109, <https://doi.org/10.1016/j.scriptamat.2015.10.025>.
- [19] J.C. Rao, H.Y. Diao, V. Ocelik, D. Vainchtein, C. Zhang, C. Kuo, Z. Tang, W. Guo, J.D. Poplawsky, Y. Zhou, P.K. Liaw, J.T.M. De Hosson, Secondary phases in AlxCoCrFeNi high-entropy alloys: an in-situ TEM heating study and thermodynamic appraisal, *Acta Mater.* 131 (2017) 206–220, <https://doi.org/10.1016/j.actamat.2017.03.066>.
- [20] C.M. Parish, J.C. Neufeld, L.J. Santodonato, M.C. Gao, M. Feynson, P.K. Liaw, R.J.K. Weber, Y. Zhang, Z. Tang, Deviation from high-entropy configurations in the atomic distributions of a multi-principal-element alloy, *Nat. Commun.* 6 (2015) 5964, <https://doi.org/10.1038/ncomms6964>.
- [21] A. Manzoni, H. Daoud, R. Völkl, U. Glatzel, N. Wanderka, Phase separation in equiatomic AlCoCrFeNi high-entropy alloy, *Ultramicroscopy* 132 (2013) 212–215, <https://doi.org/10.1016/j.ultramic.2012.12.015>.
- [22] H.Y. Diao, R. Feng, K.A. Dahmen, P.K. Liaw, Fundamental deformation behavior in high-entropy alloys: an overview, *Curr. Opin. Solid State Mater. Sci.* 21 (2017) 252–266, <https://doi.org/10.1016/j.cossms.2017.08.003>.
- [23] C.C. Tasan, D. Raabe, K.G. Pradeep, Y. Deng, Z. Li, Metastable high-entropy dual-phase alloys overcome the strength–ductility trade-off, *Nature* 534 (2016) 227, <https://doi.org/10.1038/nature17981>.
- [24] Z. Li, C.C. Tasan, K.G. Pradeep, D. Raabe, A TRIP-assisted dual-phase high-entropy alloy: grain size and phase fraction effects on deformation behavior, *Acta Mater.* 131 (2017) 323–335, <https://doi.org/10.1016/j.actamat.2017.03.069>.
- [25] Z. Tang, O.N. Senkov, C.M. Parish, C. Zhang, F. Zhang, L.J. Santodonato, G. Wang, G. Zhao, F. Yang, P.K. Liaw, Tensile ductility of an AlCoCrFeNi multi-phase high-entropy alloy through hot isostatic pressing (HIP) and homogenization, *Mater. Sci. Eng., A* 647 (2015) 229–240, <https://doi.org/10.1016/j.msea.2015.08.078>.
- [26] W.-R. Wang, W.-L. Wang, S.-C. Wang, Y.-C. Tsai, C.-H. Lai, J.-W. Yeh, Effects of Al addition on the microstructure and mechanical property of AlxCoCrFeNi high-entropy alloys, *Intermetallics* 26 (2012) 44–51, <https://doi.org/10.1016/j.intermet.2012.03.005>.
- [27] A. Marshal, K.G. Pradeep, D. Music, S. Zaefferer, P.S. De, J.M. Schneider, Combinatorial synthesis of high entropy alloys: introduction of a novel, single phase, body-centered-cubic FeMnCoCrAl solid solution, *J. Alloy. Comp.* 691 (2017) 683–689, <https://doi.org/10.1016/j.jallcom.2016.08.326>.
- [28] M.J. Yao, K.G. Pradeep, C.C. Tasan, D. Raabe, A novel, single phase, non-equiatomic FeMnNiCoCr high-entropy alloy with exceptional phase stability and tensile ductility, *Scripta Mater.* 72–73 (2014) 5–8, <https://doi.org/10.1016/j.scriptamat.2013.09.030>.
- [29] W.-R. Wang, W.-L. Wang, S.-C. Wang, Y.-C. Tsai, C.-H. Lai, J.-W. Yeh, Effects of Al addition on the microstructure and mechanical property of AlxCoCrFeNi high-entropy alloys, *Intermetallics* 26 (2012) 44–51, <https://doi.org/10.1016/j.intermet.2012.03.005>.
- [30] G. Laplanche, A. Kostka, O.M. Horst, G. Eggeler, E.P. George, Microstructure evolution and critical stress for twinning in the CrMnFeCoNi high-entropy alloy, *Acta Mater.* 118 (2016) 152–163, <https://doi.org/10.1016/j.actamat.2016.07.038>.
- [31] B. Gludovatz, E.P. George, J. Wang, M.M. Mao, Q. Yu, R.O. Ritchie, S.X. Mao, Z. Zhang, Z. Zhang, Nanoscale origins of the damage tolerance of the high-entropy alloy CrMnFeCoNi, *Nat. Commun.* 6 (2015) 10143, <https://doi.org/10.1038/ncomms10143>.
- [32] F. Otto, A. Dlouhý, C. Somsen, H. Bei, G. Eggeler, E.P. George, The influences of temperature and microstructure on the tensile properties of a CoCrFeMnNi high-entropy alloy, *Acta Mater.* 61 (2013) 5743–5755, <https://doi.org/10.1016/j.actamat.2013.06.018>.
- [33] A.M. Giwa, P.K. Liaw, K.A. Dahmen, J.R. Greer, Microstructure and small-scale size effects in plasticity of individual phases of Al0.7CoCrFeNi High Entropy alloy, *Extreme Mech. Lett.* 8 (2016) 220–228, <https://doi.org/10.1016/j.eml.2016.04.013>.
- [34] R. Raghavan, C. Kirchlechner, B.N. Jaya, M. Feuerbacher, G. Dehm, Mechanical size effects in a single crystalline equiatomic FeCrCoMnNi high entropy alloy, *Scripta Mater.* 129 (2017) 52–55, <https://doi.org/10.1016/j.scriptamat.2016.10.026>.
- [35] Y. Zou, H. Ma, R. Spolenak, Ultrastrong ductile and stable high-entropy alloys at small scales, *Nat. Commun.* 6 (2015) 7748, <https://doi.org/10.1038/ncomms8748>.
- [36] Y. Zou, S. Maiti, W. Steurer, R. Spolenak, Size-dependent plasticity in an Nb25Mo25Ta25W25 refractory high-entropy alloy, *Acta Mater.* 65 (2014) 85–97, <https://doi.org/10.1016/j.actamat.2013.11.049>.
- [37] 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, *Sci. Rep.* 6 (2016) 35863, <https://doi.org/10.1038/srep35863>.
- [38] Y.X. Ye, Z.P. Lu, T.G. Nieh, Dislocation nucleation during nanoindentation in a body-centered cubic TiZrHfNb high-entropy alloy, *Scripta Mater.* 130 (2017) 64–68, <https://doi.org/10.1016/j.scriptamat.2016.11.019>.
- [39] V. Ocelik, N. Janssen, S.N. Smith, J.T.M.D. Hosson, Additive manufacturing of high-entropy alloys by laser processing, *JOM* 68 (2016) 1810–1818, <https://doi.org/10.1007/s11837-016-1888-z>.
- [40] R. Hielscher, H. Schaeben, A novel pole figure inversion method: specification of the MTEX algorithm, *J. Appl. Crystallogr.* 41 (2008) 1024–1037, <https://doi.org/10.1107/S0021889808030112>.
- [41] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *J. Mater. Res.* 7 (1992) 1564–1583, <https://doi.org/10.1557/JMR.1992.1564>.
- [42] W.C. Oliver, G.M. Pharr, Measurement of hardness and elastic modulus by instrumented indentation: advances in understanding and refinements to methodology, *J. Mater. Res.* 19 (2004) 3–20, <https://doi.org/10.1557/jmr.2004.19.1.3>.
- [43] J.C. Rao, V. Ocelik, D. Vainchtein, Z. Tang, P.K. Liaw, J.T.M. De Hosson, The fcc-bcc crystallographic orientation relationship in AlxCoCrFeNi high-entropy alloys, *Mater. Lett.* 176 (2016) 29–32, <https://doi.org/10.1016/j.matlet.2016.04.086>.
- [44] J.C. Rao, V. Ocelik, D. Vainchtein, Z. Tang, P.K. Liaw, J.T.M. De Hosson, On the onset of nano-ordered phase distributions in high-entropy alloys, *Rev. Adv. Mater. Sci.* 48 (2017) 105–111.
- [45] A. Munitz, S. Salhov, S. Hayun, N. Frage, Heat treatment impacts the microstructure and mechanical properties of AlCoCrFeNi high entropy alloy,

- J. Alloy. Comp. 683 (2016) 221–230, <https://doi.org/10.1016/j.jallcom.2016.05.034>.
- [46] J.R. Morris, H. Bei, G.M. Pharr, E.P. George, Size effects and stochastic behavior of nanoindentation pop in, *Phys. Rev. Lett.* 106 (2011) 165502, <https://doi.org/10.1103/PhysRevLett.106.165502>.
- [47] W.A. Soer, J.T.M. De Hosson, A.M. Minor, Z. Shan, S.A. Syed Asif, O.L. Warren, Incipient plasticity in metallic thin films, *Appl. Phys. Lett.* 90 (2007) 181924, <https://doi.org/10.1063/1.2736479>.
- [48] W.A. Soer, J.T.M.D. Hosson, A.M. Minor, J.W. Morris, E.A. Stach, Effects of solute Mg on grain boundary and dislocation dynamics during nanoindentation of Al–Mg thin films, *Acta Mater.* 52 (2004) 5783–5790, <https://doi.org/10.1016/j.actamat.2004.08.032>.
- [49] J.T.M.D. Hosson, W.A. Soer, A.M. Minor, Z. Shan, E.A. Stach, S.A.S. Asif, O.L. Warren, In situ TEM nanoindentation and dislocation-grain boundary interactions: a tribute to David Brandon, *J. Mater. Sci.* 41 (2006) 7704–7719, <https://doi.org/10.1007/s10853-006-0472-2>.
- [50] K.L. Johnson, K.L. Johnson, *Contact Mechanics*, Cambridge University Press, 1987.
- [51] D.F. Bahr, D.E. Kramer, W.W. Gerberich, Non-linear deformation mechanisms during nanoindentation, *Acta Mater.* 46 (1998) 3605–3617, [https://doi.org/10.1016/S1359-6454\(98\)00024-X](https://doi.org/10.1016/S1359-6454(98)00024-X).
- [52] Y. Zhang, J.P. Liu, S.Y. Chen, X. Xie, P.K. Liaw, K.A. Dahmen, J.W. Qiao, Y.L. Wang, Serration and noise behaviors in materials, *Prog. Mater. Sci.* 90 (2017) 358–460, <https://doi.org/10.1016/j.pmatsci.2017.06.004>.
- [53] P. Rodriguez, Serrated plastic flow, *Bull. Mater. Sci.* 6 (1984) 653–663, <https://doi.org/10.1007/BF02743993>.
- [54] G. Gottstein, *Physical Foundations of Materials Science*, Springer Science & Business Media, 2013.
- [55] Y. Brechet, Y. Estrin, On the influence of precipitation on the Portevin-Le Chatelier effect, *Acta Metall. Mater.* 43 (1995) 955–963, [https://doi.org/10.1016/0956-7151\(94\)00334-E](https://doi.org/10.1016/0956-7151(94)00334-E).
- [56] J.W. Gahn, Hardening by spinodal decomposition, *Acta Metall.* 11 (1963) 1275–1282, [https://doi.org/10.1016/0001-6160\(63\)90022-1](https://doi.org/10.1016/0001-6160(63)90022-1).
- [57] M. Kato, T. Mori, L.H. Schwartz, Hardening by spinodal modulated structure, *Acta Metall.* 28 (1980) 285–290, [https://doi.org/10.1016/0001-6160\(80\)90163-7](https://doi.org/10.1016/0001-6160(80)90163-7).
- [58] A.J. Ardell, Precipitation hardening, *Metall. Trans. A* 16 (1985) 2131–2165, <https://doi.org/10.1007/BF02670416>.
- [59] M. Kato, Hardening by spinodally modulated structure in b.c.c. alloys, *Acta Metall.* 29 (1981) 79–87, [https://doi.org/10.1016/0001-6160\(81\)90088-2](https://doi.org/10.1016/0001-6160(81)90088-2).
- [60] Y. Ma, B. Jiang, C. Li, Q. Wang, C. Dong, P.K. Liaw, F. Xu, L. Sun, The BCC/B2 morphologies in Al_xNiCoFeCr high-entropy alloys, *Metals* 7 (2017) 57, <https://doi.org/10.3390/met7020057>.
- [61] J.M. Lu, Q.M. Hu, R. Yang, A comparative study of elastic constants of NiTi and NiAl alloys from first-principle calculations, *IMR OpenIR* 25 (2009). <http://ir.imr.ac.cn/handle/321006/32149>. (Accessed 24 November 2017).
- [62] R.J. Wasilewski, Elastic constants and youngs modulus of nial, *Aime Met. Soc. Trans.* 236 (1966) 455–457.
- [63] N.I. Medvedeva, O.N. Mryasov, Y.N. Gornostyrev, D.L. Novikov, A.J. Freeman, First-principles total-energy calculations for planar shear and cleavage decohesion processes in B2-ordered NiAl and FeAl, *Phys. Rev. B* 54 (1996) 13506–13514, <https://doi.org/10.1103/PhysRevB.54.13506>.
- [64] L.M. Brown, R.K. Ham, D.-P. Interactions, *Strengthening Methods in Crystals*. a. Kelly and R.B. Nicholson, Elsevier, Amsterdam, 1971.
- [65] E. Nembach, G. Neite, Precipitation hardening of superalloys by ordered γ' -particles, *Prog. Mater. Sci.* 29 (1985) 177–319, [https://doi.org/10.1016/0079-6425\(85\)90001-5](https://doi.org/10.1016/0079-6425(85)90001-5).
- [66] L. Wang, H. Bei, T.L. Li, Y.F. Gao, E.P. George, T.G. Nieh, Determining the activation energies and slip systems for dislocation nucleation in body-centered cubic Mo and face-centered cubic Ni single crystals, *Scripta Mater.* 65 (2011) 179–182, <https://doi.org/10.1016/j.scriptamat.2011.03.036>.
- [67] A.C. Lund, C.A. Schuh, J.K. Mason, Quantitative insight into dislocation nucleation from high-temperature nanoindentation experiments, *Nat. Mater.* 4 (2005) 617, <https://doi.org/10.1038/nmat1429>.
- [68] M. Dao, L. Lu, R.J. Asaro, J.T.M. De Hosson, E. Ma, Toward a quantitative understanding of mechanical behavior of nanocrystalline metals, *Acta Mater.* 55 (2007) 4041–4065, <https://doi.org/10.1016/j.actamat.2007.01.038>.
- [69] J.R. Greer, J.T.M. De Hosson, Plasticity in small-sized metallic systems: intrinsic versus extrinsic size effect, *Prog. Mater. Sci.* 56 (2011) 654–724, <https://doi.org/10.1016/j.pmatsci.2011.01.005>.
- [70] B.H. Tian, Y.G. Zhang, C.Q. Chen, Serrated flow related to shearing of particles in binary Al–Li single crystals, *Mater. Sci. Eng., A* 254 (1998) 227–233, [https://doi.org/10.1016/S0921-5093\(98\)00692-3](https://doi.org/10.1016/S0921-5093(98)00692-3).
- [71] M. Pozuelo, Y.W. Chang, J. Marian, J.M. Yang, Serrated flow in nanostructured binary Mg–Al alloys, *Scripta Mater.* 127 (2017) 178–181, <https://doi.org/10.1016/j.scriptamat.2016.09.019>.
- [72] D. Choudhuri, S.A. Mantri, T. Alam, S. Banerjee, R. Banerjee, Precipitate-dislocation interaction mediated Portevin-Le Chatelier-like effect in a beta-stabilized Ti–Mo–Nb–Al alloy, *Scripta Mater.* 124 (2016) 15–20, <https://doi.org/10.1016/j.scriptamat.2016.06.043>.
- [73] K.S. Lee, B. Bae, J.-H. Kang, K.R. Lim, Y.S. Na, Multi-phase refining of an AlCoCrFeNi high entropy alloy by hot compression, *Mater. Lett.* 198 (2017) 81–84, <https://doi.org/10.1016/j.matlet.2017.03.181>.
- [74] K.S. Lee, J.-H. Kang, K.R. Lim, Y.S. Na, Influence of compressive strain on the microstructural evolution of an AlCoCrFeNi high entropy alloy, *Mater. Char.* 132 (2017) 162–168, <https://doi.org/10.1016/j.matchar.2017.08.010>.