Mechanical properties, microstructure and thermal stability of a nanocrystalline CoCrFeMnNi high-entropy alloy after severe plastic deformation

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ABSTRACT
An equiatomic CoCrFeMnNi high-entropy alloy (HEA), produced by arc melting and drop casting, was subjected to severe plastic deformation (SPD) using high-pressure torsion. This process induced substantial grain refinement in the coarse-grained casting leading to a grain size of approximately 50 nm. As a result, strength increased significantly to 1950 MPa, and hardness to \(520 \text{ HV}\). Analyses using transmission electron microscopy (TEM) and 3-dimensional atom probe tomography (3D-APT) showed that, after SPD, the alloy remained a true single-phase solid solution down to the atomic scale. Subsequent investigations characterized the evolution of mechanical properties and microstructure of this nanocrystalline HEA upon annealing. Isochronal (for 1 h) and isothermal heat treatments were performed followed by microhardness and tensile tests. The isochronal anneals led to a marked hardness increase with a maximum hardness of \(630 \text{ HV}\) at about 450 °C before softening set in at higher temperatures. The isothermal anneals, performed at this peak hardness temperature, revealed an additional hardness rise to a maximum of about 910 HV after 100 h. To clarify this unexpected annealing response, comprehensive microstructural analyses were performed using TEM and 3D-APT. New nano-scale phases were observed to form in the originally single-phase HEA. After times as short as 5 min at 450 °C, a NiMn phase and Cr-rich phase formed. With increasing annealing time, their volume fractions increased and a third phase, FeCo, also formed. It appears that the surfeit of grain boundaries in the nanocrystalline HEA offer many fast diffusion pathways and nucleation sites to facilitate this phase decomposition. The hardness increase, especially for the longer annealing times, can be attributed to these nano-scaled phases embedded in the HEA matrix. The present results give new valuable insights into the phase stability of single-phase high-entropy alloys as well as the mechanisms controlling the mechanical properties of nanostructured multiphase composites.

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1. Introduction

Compositionally complex alloys consisting of five or more principal elements, frequently referred to as high-entropy alloys (HEAs), have received considerable attention in the material science community in the last few years [1–3]. In the huge pool of alloy systems that have been investigated, only a minority of alloys crystallize as pure single-phase solid solutions e.g., [4], which can be a desirable feature for achieving certain physical and mechanical properties. An example of such a single-phase HEA is the equiatomic CoCrFeMnNi alloy first reported by Cantor et al. [5]. Even though the elements in this five-element alloy possess different crystal structures, it crystallizes as a single-phase face-centered cubic (fcc) solid solution [6]. Its mechanical properties have been recently studied [7–16]. Among its interesting features is the observation that the alloy shows a strong increase of yield strength with decreasing temperature [7,9], especially in the cryogenic range, which is a characteristic of pure body-centered cubic (bcc) metals and some binary fcc alloys but not pure fcc metals. The mechanism responsible for this phenomenon is still
under discussion. Surprisingly, along with the increase of strength, ductility also improves significantly at low temperatures [7,9], which was attributed to deformation induced nano-twinning [7] and the resulting increase of the work hardening rate which postpones necking instability [7,9]. In addition, the fracture resistance of this alloy has been found to be unaffected (or even rises slightly by some measures) at cryogenic temperatures [16]. Complete to the exceptional properties at low temperatures, the microstructure has been reported to be thermally stable at elevated temperatures [6].

A common method for the production of wrought fcc HEAs for mechanical property characterization involves melting and casting of the pure elements followed by rolling and recrystallization [7]. With this processing route, the smallest achievable grain size, which is preferably small for optimal mechanical properties, is determined by the degree of deformation during rolling. Because of this limitation of standard thermomechanical treatments, the entire body of research on single-phase HEAs has so far been on materials with grain sizes in the micrometer range or larger. A well-established approach to achieve significantly smaller grain sizes, is provided by methods of severe plastic deformation (SPD) [17–19]. These methods allow deformations far beyond those possible by cold rolling and can reduce grain sizes down to the nanoscale. The SPD process, which is preferably small for optimal mechanical properties, is determined by the degree of deformation during rolling. Because of this limitation of standard thermomechanical treatments, the entire body of research on single-phase HEAs has so far been on materials with grain sizes in the micrometer range or larger. A well-established approach to achieve significantly smaller grain sizes, is provided by methods of severe plastic deformation (SPD) [17–19]. These methods allow deformations far beyond those possible by cold rolling and can reduce grain sizes down to the nanoscale. The SPD process, which is capable of visualizing re-distributions of elements and the formation of new phases on the atomic scale.

2. Experimental

For the synthesis of the CoCrFeMnNi HEA, high-purity elements (at least 99.9 wt%) were arc melted and drop cast under pure Ar atmosphere into cylindrical copper molds 25.4 mm in diameter and 127 mm long. The drop-cast ingots were encapsulated, evacuated in quartz ampules and homogenized for 48 h at 1200 °C. Further details of the melting and casting process can be found elsewhere [7]. Afterwards the material was subjected to high pressure torsion (HPT). An introduction to this processing technique is given in [24]. For the HPT process, disks with a diameter of 8 mm and an initial thickness of 0.8 mm were cut from the cast and homogenized ingot. During HPT, the shear strain, \( \gamma \), along the radius, \( r \), is given by:

\[
\gamma = \frac{2\pi r}{t} n,
\]

where \( t \) is the thickness of the disk and \( n \) the number of rotations. The process was conducted at room temperature at a nominal pressure of 7.8 GPa and a rotational speed of 0.2 rotations/min for various values of \( n \). Specimens subjected to 5 rotations were used for isochronal heat treatments for 1 h and isothermal heat treatments at 450 °C.

Vickers micro-hardness measurements were conducted with a microhardness tester from Buehler (Micromet 5104) at a load of 1000 gf and dwell times of 15 s. Tensile tests were performed with dog-bone specimens having a gage length of 2.5 mm and a square cross-section of ~0.3 mm². The tests were conducted at room temperature on a tensile testing machine from Kammrath and Weiss with a crosshead speed of 2.5 μm/s.

Microstructural characterization and fractographic studies were carried out with a scanning electron microscope (SEM, Zeiss 1525). Standard bright-field images and diffraction patterns were obtained using a transmission electron microscope from Philips (CM12) and STEM images were recorded using an image-side C₂-corrected JEOL 2100F. For TEM specimen preparation, conventional electropolishing methods or Ar-ion milling were employed depending on the microstructure. Further in-depth microstructural investigations were made with 3 dimensional atom probe tomography (3D-APT) using the LEAP 3000X HR. The APT specimens were prepared by cutting rod-like specimens from selected microstructural states followed by electropolishing to pre-sharpen the tips. In addition, ion milling with a FEI Versa 3D DualBeam (FIB/SEM) workstation was employed to get the final shape of the specimens. The measurements were performed in voltage mode with a pulse fraction of 20%, a pulse rate of 200 kHz and a temperature of 60 K. The reconstructions were performed with the visualization and analysis software IVAS, version 3.6.8 from CAMECA.

3. Results

3.1. Mechanical and microstructural changes during SPD

In Fig. 1a the hardness evolution along the disk radius as a function of the number of rotations is presented. The data from 4 equivalent radial positions, see inset in Fig. 1b, were averaged and their standard deviations used as an indicator of the error. The undeformed specimen has a hardness of about 160 HV. Pre-loading of the specimen at a nominal pressure of 7.8 GPa (denoted as 0 rotations) produces a marked hardness increase in the outer edge region. There the degree of deformation is somewhat higher compared to the center of the disk due to the pressure distribution in the tool. With increasing number of rotations the hardness level further increases, which can be linked to severe grain fragmentation. After just 1/4 rotation the hardness begins to saturate at the edge. After 5 rotations a broad plateau in hardness is reached, which begins at a radius of about 1 mm from the center and extends to the outer edge of the disk. To take advantage of this pronounced plateau, only disks deformed to 5 rotations were used for all subsequent investigations. The plateau in hardness, with an average value of about 520 HV, indicates a saturation in grain refinement. The minimum grain size in this region is reached after further increases, which can be linked to severe grain fragmentation. After just 1/4 rotation the hardness begins to saturate at the edge. After 5 rotations a broad plateau in hardness is reached, which begins at a radius of about 1 mm from the center and extends to the outer edge of the disk. To take advantage of this pronounced plateau, only disks deformed to 5 rotations were used for all subsequent investigations. The plateau in hardness, with an average value of about 520 HV, indicates a saturation in grain refinement. The minimum grain size in this region is reached after
temperatures during plane-strain multi-pass rolling [8]. The relatively early onset of room-temperature twinning in this study can be explained by the very coarse grain size of our starting material, which is expected to have a higher propensity for twinning than finer grained metals [25]. Similar observations were made regarding twinning being the prevalent deformation mode during grain refinement with SPD in austenitic steels [26]. Deformation twins were also frequently observed in CuZn alloys [27], which are examples of low stacking fault energy materials.

3.2. Saturation microstructure

The saturation microstructure in Fig. 2f was further investigated by TEM along the axial direction as shown in Fig. 3a. In general, the images for this microstructural state tend to show unclear (blurry) structures in which the boundaries are ill defined and difficult to discern. This is often associated with internal stresses or strains related to the non-equilibrium nature of grain boundaries in severely plastically deformed materials [28]. Only several grains could be clearly discriminated after inspection of a large number of images on the basis of which an average grain diameter of ~50 nm was estimated. Twins were seldom found, as one isolated example in the center of the image illustrates. The diffraction pattern (Fig. 3b) shows Debeye rings with a sequence that is consistent with a single-phase fcc structure for the severely plastically deformed HEA. A calculation of the lattice constant yields a value of ~3.6 Å, which is in good accordance with measurements using X-ray diffraction for the coarse-grained state [29].

To illustrate the chemical composition and homogeneity of the structure, 3D-APT results are presented in Fig. 4a. These single-element images, as well as the chemical compositions along the long axis of the specimen, Fig. 4b, verify the single-phase solid solution character of the material with no observable inhomogeneities or clusters and a somewhat decreased Mn level compared to the nominal equiatomic composition. The discrepancy in the Mn level compared to the nominal composition might be a consequence of the high vapor pressure of Mn leading to evaporation of the element during the casting and homogenization process [30]. Based on the grain size estimated above from the TEM analyses, the volume analyzed by 3D-APT should contain several grain boundaries. Since they do not seem to be decorated by any specific species they cannot be visualized by the 3D-APT technique. This also means that no grain boundary segregants are present in the SPD state.

3.3. Hardness evolution during annealing experiments

In Fig. 5a, the results of the isochronal heat treatments (1 h) are shown. Beginning from the hardness of the SPD state (~520 HV), a clear rise in hardness occurs with a maximum hardness of 630 HV at a temperature of 450 °C. At higher annealing temperatures the hardness decreases. To shed light on the kinetics of hardness evolution, isothermal heat treatments were also performed for times up to 200 h at the annealing temperature where hardness was found to be a maximum in the isochronal anneals. The results, shown in Fig. 5b, indicate a continuous increase in hardness from the SPD state to a peak hardness of ~910 HV after an annealing time of 100 h before the hardness starts to decrease again.

3.4. Microstructural analyses of annealed specimens

To correlate the hardness changes with the microstructure, 3D-APT and TEM analyses were performed on specimens annealed at 450 °C for selected times. The chosen temperature corresponds to that at which peak hardness was observed in the isochronal experiments. In Fig. 6 the 3D-APT results are presented showing
the presence of new phases besides the solid solution phase of the base HEA (Fig. 4a). These new phases will be denominated by their main constituents in the following discussion. After very short anneals (5 min), a phase rich in Mn and Ni and a second phase rich in Cr were found embedded in the HE phase, see Fig. 6a. The estimated compositions of these phases within the shown iso-concentration surfaces are summarized in Table 1. After a 1-h anneal, Fig. 6b, the same phases are present as after the 5-min anneal but their volume fractions increased markedly, as shown in Table 1. After 15 h the hardness increased considerably, see Fig. 5b. The corresponding 3D-APT reconstruction, Fig. 6c, reveals the formation of an additional phase consisting mainly of Fe and Co and a further increase in the volume fractions of the first two phases. More or less independent of the annealing time the composition of the MnNi phase remains roughly constant, whereas the Cr content in the Cr phase increases with increasing annealing time. Even though the hardness continues to increase after 15 h no further 3D-APT measurements were performed on these samples due to their high intrinsic brittleness which resulted in failure during several preparation attempts.

TEM investigations of the same microstructural states as above allowed further structural information to be obtained for the newly formed phases and the results are compiled in Fig. 7. For very short anneals, Fig. 7a, the microstructure appears to become clearer compared to the one presented earlier for the SPD state (Fig. 3a); however, in the diffraction pattern, Fig. 7b, no significant changes can be seen (compared to Fig. 3b), even though the 3D-APT results clearly show the formation of new phases (Fig. 6a). This is due to their very small volume fractions (Table 1). After a 1-h anneal, a slight coarsening of the structure is visible in Fig. 7c and very weak additional reflections can be seen in the diffraction pattern, Fig. 7d. With a further increase in annealing time (to 15 h) the microstructure becomes coarser, Fig. 7e, while at the same time hardness increases (Fig. 5b). Furthermore, there is a pronounced change in the diffraction pattern from continuous to discontinuous rings.

Fig. 2. Microstructural evolution in HPT disks investigated with SEM using back-scattered electron contrast. (a) Schematic diagram showing the principal viewing direction for SEM and TEM analyses. (b) Undeformed coarse-grained initial structure of the cast alloy. (c) Deformation structure of the HPT disk after 1/8 of a rotation with the dashed circle showing the center of the disk. (d) Deformation structure with multiple twinning systems after a shear strain of γ ~ 2.4. (e) Fragmentation of the twinned structure at higher strains, γ ~ 4.0. (f) Final saturation microstructure (γ ~ 50).

Fig. 3. Microstructure of the severely plastically deformed CoCrFeMnNi alloy. (a) STEM image of the saturation microstructure (b) Detail of representative diffraction pattern displaying fcc reflections.
comprising individual spots accompanied with the formation of additional Debye-Scherer rings compared to the SPD and 5-min-annealed states. The additional rings can be correlated with a bcc phase having a lattice constant of approximately 2.9 Å. The precision with which lattice constants can be determined using simple diffraction patterns is undeniably lower compared to other techniques, which makes an unambiguous identification based on just the electron diffraction pattern difficult. However, the calculated value is close that of pure Cr, which has a lattice constant of 2.88 Å [31], suggesting that these additional rings are very likely due to the Cr-rich phase, which itself is not pure but alloyed with other species (Table 1) that likely alter its lattice constant.

A closer look at the pattern in Fig. 7f reveals that there are two distinct sets of fcc rings. The second fcc set has a somewhat larger lattice constant of ~3.8 Å. To explain the possible origin of this set, we consulted the binary Mn–Ni phase diagram [32]. It does not reveal a disordered fcc structure in the middle of the phase diagram around the composition shown in Table 1. Rather, the α-MnNi phase in the diagram has the ordered L1₀ structure. The presence of other alloying elements (Cr, Fe, Co) in our Mn–Ni phase, see Table 1, might have induced disorder in what would have been an ordered phase in the pure Mn–Ni binary system. Assuming this is true in the present case, the disordered MnNi(Cr, Fe, Co) phase would be equivalent to a fcc phase giving rise to the second set of fcc rings. Lastly, a FeCo phase was identified by 3D-APT whose presence should, in principle, be found in the diffraction pattern as well. However, the lattice constant of such a phase is expected to be ~2.85 Å based on the binary Fe–Co system [33]. The diffraction rings stemming from this phase would be very close to those of the previously mentioned Cr phase (lattice constant, ~2.9 Å) making them virtually indistinguishable. Despite this uncertainty in phase identification based on the diffraction patterns, it is worth noting that the 15-h specimen becomes strongly magnetic, which is likely due to the formation of the FeCo phase.

3.5. Tensile tests

In Fig. 8, results of representative tensile tests performed after different annealing treatments are shown. Due to the restricted sample size only the displacement of the stroke (and not strain
work-hardening is restored, which is typical for this alloy in the coarse-grained state [7].

4. Discussion

4.1. Thermal stability and decomposition of the NC alloy

In view of the existing literature, the most significant phenomenon observed in this study was the decomposition tendency of the CoCrFeMnNi HEA upon annealing after SPD. In preceding publications on coarser-grained HEAs with similar composition, a true solid solution down to the atomic scale was found [34] as well as good high-temperature stability with no tendency of decomposition [6]. In this study, by contrast, the originally single-phase HEA with NC grains transforms relatively rapidly into a nanostructured multiphase composite consisting of several different new phases during annealing. As discussed later, a possible reason for this difference is that the nanocrystalline structure of the present alloy enhances overall diffusion by providing an abundance of grain boundaries. Otherwise, as shown by Tsai et al. [35], diffusion in this CoCrFeMnNi HEA is expected to be sluggish since the diffusivities of its constituent elements are smaller than their values in pure metals as well as in alloys consisting of fewer constituents than the quinary.

At the beginning a MnNi phase and a Cr-rich phase are formed, see Fig. 6a and b and after longer annealing times a FeCo phase could be detected, Fig. 6c. The chronological sequence of these phases can be rationalized by considering their relative diffusivities. The magnitude of the diffusion coefficients of the individual elements in the CoCrFeMnNi alloy was investigated by Tsai et al. [35]. They found a similar ordering of the diffusion coefficients as that of the pure metals [36]. The element that diffuses fastest at a fixed temperature is Mn, which is consistent with the formation of the MnNi phase first. The second phase to form has a very high Cr concentration, which has the next highest diffusion coefficient after Mn. Only after longer annealing times does the FeCo phase form, which consists of elements that have the next highest diffusion coefficients after Mn and Cr. These three new phases together with the primary fcc matrix phase form a multiphase NC microstructure.

Unlike previous work in which this HEA was found to be thermally stable at times up to three days [6], phase decomposition occurs in the SPD-deformed HEA at much shorter times. This can be partly attributed to the chosen annealing temperature regime. The previous microcrystalline samples were processed by cold rolling followed by annealing in a temperature range somewhat above the recrystallization temperature, which is about 800 °C depending on the degree of pre-deformation [37] and in this temperature regime a pure single-phase structure is formed. Zhang et al. [38] used the CALPHAD (Calculation of Phase Diagrams) approach to calculate phase diagrams for such multicomponent alloys and predicted a single-phase fcc-structure for temperatures above 600 °C. In this study a lower temperature regime for annealing was targeted to avoid recrystallization or grain growth, which would otherwise weaken the beneficial effect of grain refinement on strength. Of relevance to the annealing temperature range used in the present study is Zhang et al.’s prediction of a multiphase mixture below 600 °C. For comparison, the microstructures obtained by annealing for 1 h at temperatures above 600 °C are presented in Fig. 9. In contrast to the SPD state and those produced by annealing at 450 °C, substantial grain growth can be observed at higher temperatures. More importantly, another phase or phases were still found after 1-h anneals above 600 °C. As an example the microstructure annealed at 700 °C is presented in Fig. 8a, where second-phase particles (encircled) can be seen. Due to their

Table 1

Summary of 3D-APT results showing the estimated chemical compositions and volume fractions of the phases formed in the originally single-phase NC HEA after annealing for various times at 450 °C. The main constituents of each individual phase are shown in bold font. Due to the small analyzed volumes the values of the volume fraction provide general trends and not exact values.

| Annealing state | Phase | Mn (at.%) | Ni (at.%) | Cr (at.%) | Fe (at.%) | Co (at.%) | Vol% |
|-----------------|-------|-----------|-----------|-----------|-----------|-----------|------|
| 5 min           | NiMn  | 43.5      | 46.2      | 2.8       | 2.7       | 4.7       | 0.6  |
|                 | Cr    | 6.2       | 1.8       | 71        | 13.6      | 7.3       | 0.9  |
| 1 h             | NiMn  | 46.0      | 45.7      | 2.0       | 2.0       | 4.2       | 9.1  |
|                 | Cr    | 5.0       | 1.6       | 74.2      | 12.1      | 6.8       | 1.3  |
| 15 h            | NiMn  | 44.1      | 46.2      | 2.6       | 2.3       | 4.2       | 16.9 |
|                 | Cr    | 3.4       | 0.4       | 81.8      | 9.6       | 4.1       | 13.5 |
|                 | FeCo  | 5.7       | 1.7       | 0.3       | 46.7      | 45.3      | 27.3 |
small size it was not possible to analyze them in the SEM using energy dispersive X-ray spectroscopy. Nevertheless, it is reasonable to assume that they are similar to the phases found by 3D-APT and discussed earlier, Fig. 6. At the higher annealing temperature of 750 °C, they can be clearly seen to be situated at grain boundaries and triple junctions, Fig. 9b. Interestingly, subjecting the material to an even higher annealing temperature of 800 °C for 1 h leads once again to a pure single-phase material, but with a substantially increased grain size of about 10 μm, Fig. 9c. This illustrates clearly that similar heat treatments as those used for heavily cold rolled materials [37], which were used to obtain a fully recrystallized structure with microcrystalline grain sizes, produce similar single-phase microstructures.

Besides the annealing temperature being a factor, the intrinsic nature of NC metals also contributes to the kinetics of phase formation: the 3D-APT measurements together with the hardness measurements have clearly demonstrated that these phases appear very quickly, after just a few minutes of annealing. This fast formation of new phases can be understood by considering the role of grain boundaries in diffusion-controlled precipitation and phase formation processes in NC metals, see [39,40]. The total grain boundary area drastically increases by lowering the grain size. These boundaries can serve as fast diffusion pathways and represent energetically preferred nucleation sites for the formation of new phases with much faster kinetics than in coarser grained alloys where bulk diffusion prevails. In this context, the significant contribution of triple junctions in NC metals should be mentioned, which has been proposed to allow increased diffusion by short circuit diffusion [41]. This is supported by the micrographs in Fig. 9a and b showing the presence of second phase particles at triple junctions. However, it should be kept in mind that these micrographs depict the condition for high annealing temperatures, where the initial NC-structure has already coarsened. Focusing on the NC-structure, the diffusion coefficients measured for bulk diffusion in microcrystalline materials [35] play only a minor role in the NC state and a much larger diffusivity mainly triggered by grain boundary diffusion should be expected. It should be noted, however, that if the existence of these phases is thermodynamically predicted based on a minimum of the Gibbs free energy, they would also occur in coarser grained samples subjected to similar heat treatments. The only expected difference is the time scale that is needed to allow sufficient diffusion in the larger grain-size regime.

Fig. 7. Examples of the microstructures of differently annealed samples and their representative diffraction patterns. (a and b) 5-min anneal, (c and d) 1-h anneal, (e and f) 15-h anneal. Note that for 5-min and 1-h anneals STEM images are shown whereas for the 15-h specimen, due to the strong magnetism of the structure, a conventional bright-field image is presented with a slightly different magnification.

Fig. 8. Results of tensile tests performed in the different annealed states. (a) Examples for annealing treatments performed at the peak temperature for the isochronal treatment. (b) Annealing treatments above the peak temperature.

264 B. Schuh et al. / Acta Materialia 96 (2015) 258–268
Although the formation of these new phases is a rather new phenomenon in this HEA, other so-called HEAs exhibit a two- or multi-phase structure quite frequently [4]. Even in the CoCrFeMnNi alloy, the replacement of a single element by another or the removal of a specific species can lead to phase separation [42–44]. This suggests that single-phase HEAs are likely restricted to narrow compositional ranges. The current study has expanded our understanding of single-phase HEAs by uncovering previously unreported thermal aspects of phase stability. Although recrystallization temperatures around 800 °C lead to a single-phase material, this study shows that subsequent thermal exposures in the range of 450–750 °C during application could lead to long-term structural modifications combined with mechanical and physical property changes. This behavior could even be true for lower temperatures as a hardness increase was detected for temperatures below 450 °C, see Fig. 5a. SPD provides a convenient way to probe these changes by accelerating the phase decomposition process and opening a window into the long-term phase stability of conventional-grain-size alloys.

4.2. Strengthening mechanisms in the NC alloy

Equally intriguing as the above decomposition behavior is the substantial increase in hardness upon annealing. At first glance, it is reasonable to suppose that this behavior is simply linked to the formation of the new phases as is the case in some other HEAs. For example, in a Al_{0.3}CrFe_{1.5}MnNi alloy an increase in hardness has been associated with the formation of new phases after heat treatment where the entire matrix undergoes a phase transformation into a significantly harder phase [45]. Similarly, in an Al_{0.3}CoCrFeNi alloy subjected to SPD and annealed for different temperatures the hardness increase has also been associated with the formation of a hard secondary phase [46]. However, we believe that the hardening mechanism in the present NC HEA is more complicated as discussed below.

Due to energetic considerations, the nucleation sites for the new phases found by 3D-APT can be assumed to lie on the grain boundaries of the matrix phase. The resulting clusters or second phases that form at these sites can hinder dislocation emission and motion at grain boundaries. Such a grain boundary segregation based strengthening mechanism has been proposed before to explain the origin of the unusually high strength in SPD-processed Al alloys [47] and austenitic steels [48]. In the NC HEA, after very short anneals, the typical dimensions of these new phases are similar to those of the primary phase, i.e., several tens of nanometers, see Fig. 6b, and the hardness continuously increases as shown in Fig. 5b. This means that the strengthening cannot be exclusively explained by segregation at grain boundaries. For classical precipitation hardening, the precipitates are situated within individual grains and have to remain small compared to the grain size to be effective obstacles for dislocation motion.

A further mechanism that can contribute to strengthening is a reduction of the dislocation density upon annealing [49,50]. The NC structure provides a large fraction of grain boundaries that can absorb dislocations during annealing. To realize plastic flow after annealing, new dislocation sources have to be activated. Especially in the NC grain size regime, the emission of dislocations from grain boundaries becomes significant [51]. In SPD structures, grain boundaries are often considered to be in a “non-equilibrium” state. This is a possible reason for the slightly blurry appearance of the microstructure seen in conventional TEM investigations [28], as well as in the present study, see Fig. 3a. These boundaries may relax during annealing necessitating an increased stress level compared to the SPD state for the emission and accommodation of dislocations at these recovered boundaries.

Another contribution to the strength can be envisaged by considering the microstructure as a nano-composite consisting of several phases differing markedly in their intrinsic strength. Two of the newly formed phases have an intermetallic character, which is commonly thought to provide high strength. As such, these intermetallic phases would be expected to yield at higher stress levels and partly constrain the deformation of the surrounding softer matrix resulting in an increased global strength of the alloy. Unfortunately, due to their small size, they cannot be individually tested, even with nano-indentation, so it remains unverified at present. Regardless, this composite based explanation can only hold when the volume fractions of the newly formed phases become large, see Table 1. For the early stages of hardening the aforementioned recovery but also the segregation at grain boundaries seem to be significant factors in the hardness increase.

There is a recent example in the literature that is suggestive of possible phase formation processes even in the coarse-grained version of this CoCrFeMnNi HEA [37]. A similar hardness increase as in the present study was observed after cold rolling and annealing in a similar temperature range below the recrystallization temperature. Due to a lower degree of deformation the absolute hardness values after deformation were lower and the relative hardness increase upon annealing less pronounced. An explanation for the slight hardness increase remained an open question in that paper [37] but it might be related to the results obtained by 3D-APT in this study.

4.3. Impact of SPD and annealing on ductility

Ultrafine-grained (UFG) alloys obtained by various SPD techniques frequently show unprecedented mechanical properties [52]. Even when deformation related properties such as ductility...
are inferior compared to those of the coarse-grained starting materials, different strategies have been developed to regain ductility in such alloys. For example, with heat treatments the ductility can be markedly improved while keeping the loss of strength at an acceptable level [53]. However, applying this strategy to the present NC HEA leads to a further reduction of ductility, see Fig. 8a. The deterioration can also be seen on typical fractographs, presented in Fig. 10. Whereas the SPD state, Fig. 10a, is composed of dimples in the size range of several hundred nanometers, the fracture appearance becomes gradually more brittle along with grain boundary fracture the longer the material is annealed, Fig. 10b and c. The observed embrittlement is a consequence of the multiphase-composite formation. By increasing the annealing temperature, substantial grain growth occurs (Fig. 9), accompanied with a decrease in strength. Concurrently, there is a beneficial increase in ductility, which is evident in the tensile test results, Fig. 8b. In addition, the fractographs display ductile dimpled fracture for the different elevated annealing temperatures, Fig. 10d and e. The 600 and 700 °C annealed specimens, Fig. 10d and e, show a dense population of dimples and their diameter is restricted by the average particle distance. Those particles are recognizable on the micrographs in Fig. 9 for anneals below 800 °C as well and originate from the phase decomposition during annealing. For anneals above 800 °C the high density of particles has vanished both on the fracture surface, Fig. 10f, as well as in the microstructure, Fig. 9c. The considerably larger dimples are initiated at the remaining inclusions, which can be even found in very pure materials elongated to fracture.

For possible future applications of NC HEAs an optimization of strength and ductility has to be strived for. To accomplish that, short-term anneals at temperatures above the peak-hardening temperature seem to be promising. By minimizing the temperature exposure, the NC grains may remain small, which is a pre-condition for keeping the strength at a reasonable level. Simultaneously, the decomposition leading to new phase formation could be suppressed when the target temperature corresponds thermodynamically to a single phase state, which may be around 800 °C in this particular HEA. A higher annealing temperature, however, would accelerate grain growth as well. Therefore, in future research, it is crucial to carefully investigate how to balance annealing temperature and time to obtain optimum strength and ductility.

5. Summary and conclusions

An equiatomic CoCrFeMnNi high-entropy alloy produced by arc melting and drop casting was homogenized and subjected to severe plastic deformation using high-pressure torsion. As a result, the microstructure was refined to a grain size of approximately 50 nm along with an exceptional increase of strength. In the as-processed NC state, the true solid solution, single-phase, fcc structure of this HEA was maintained. The material was then used for subsequent annealing treatments and the main findings can be summarized as follows:

(i) Isochronal heat treatments for 1 h lead to a significant hardening at temperatures to 450 °C before softening sets in for higher annealing temperatures.
(ii) Isothermal heat treatments at the peak-hardening temperature of 450 °C result in a continuous increase of hardness up to approximately 100 h.
(iii) The hardening behavior, especially for the longer annealing times, can be mainly attributed to the formation of a nanostructured multiphase microstructure, consisting of a MnNi phase, a Cr-rich phase, and a Fe–Co phase embedded in the HE matrix.
(iv) This phase decomposition from the initial solid solution state occurs relatively fast, in as little as 5 min at 450 °C for the formation of the NiMn and Cr phases, and somewhat longer (~15 h) for the formation of the FeCo phase at 450 °C.
(v) The nanocrystalline grain size of the SPD processed HEA appears to facilitate these phase transformations owing to
the large number of grain boundaries serving as fast diffusion pathways and preferential nucleation sites for the formation of new phases.

(vi) In tensile tests, exceptional strength levels can be achieved, however the ductility is low. To overcome this drawback, short-term anneals above the isochronal hardness maximum are proposed to maintain the strength at a reasonable level while ductility is regained.

This observed phase instability of the CoCrFeMnNi (Cantor) alloy, which is often cited in the literature as one of the few true solid solution high-entropy alloys, suggests that careful consideration needs to be given in the future to the application temperature, possibly even in the case of coarser grained alloys that might be exposed for long times.

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