Nanoindentation testing as a powerful screening tool for assessing phase stability of nanocrystalline high-entropy alloys

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Abstract

The equiatomic high-entropy alloy (HEA), CrMnFeCoNi, has recently been shown to be microstructurally unstable, resulting in a multi-phase microstructure after intermediate-temperature annealing treatments. The decomposition occurs rapidly in the nanocrystalline (NC) state and after longer annealing times in coarse-grained states. To characterize the mechanical properties of differently annealed NC states containing multiple phases, nanoindentation was used. The results revealed besides drastic changes in hardness, also for the first time significant changes in the Young's modulus and strain rate sensitivity. Nanoindentation of NC HEAs is, therefore, a useful complementary screening tool with high potential as a high throughput approach to detect phase decomposition, which can also be used to qualitatively predict the long-term stability of single-phase HEAs.

Keywords: Nanoindentation; high-entropy alloys; severe plastic deformation; high-pressure torsion; phase stability; nanocrystalline

Introduction

The Cantor alloy, an equiatomic CrMnFeCoNi alloy, is one of the few multi-principal-element alloys, or HEAs, that is a single-phase solid solution at room temperature after elevated temperature homogenization [1,2]. Since the first report of its existence in 2004 [3] the mechanical and physical properties has been thoroughly investigated[4–16] along with many other systems[17,18]. Recent studies have concentrated on phase stability as a function of temperature and revealed the formation of metallic and intermetallic phases at temperatures below ~ 800 °C. The first study [19] to demonstrate decomposition in this HEA dealt with its nanocrystalline (NC) state in which the decomposition occurred fast, within minutes. Subsequent reports dealt with larger grain sizes in the millimeter range (referred to as coarse-grained (CG) materials here) where the second phases were observed after much longer times [20,21]. The decomposition into a multiphase structure has the potential to significantly affect mechanical properties. For example, in the NC state, which has a relatively high strength even before annealing, the decomposition was accompanied by an increase of strength and decrease of ductility [19]. However, the impact on other important properties, such as Young's modulus or strain rate sensitivity (SRS), has not yet been investigated. The effects of decomposition on the mechanical properties of the CG HEA have not been reported, but it is a concern since grain boundary precipitation of deleterious intermetallic phases could potentially cause embrittlement.

For studying these decomposition effects mainly advanced microscopy techniques such as SEM (scanning electron microscopy) with BSE (backscattered electron) contrast, TEM (transmission electron microscopy) or even more localized three-dimensional APT (atom probe tomography) are used. Even though these methods are required to gain important insights into the complex microstructures, sample preparation, especially for TEM and APT, is time consuming. Moreover, the large compositional space of these new class of multi-principal element alloys also requires new, high throughput approaches, which can accelerate the discovery and development of alloy compositions with interesting and promising material properties [22–24] especially when a single-phase character for a certain application temperature is targeted. Therefore, a simple method would be beneficial that allows a faster and reliable screening and evaluation of possible decomposition effects in single-phase HE-alloys before advanced microstructural analysis methods are applied.

Here we evaluate the potential of nanoindentation testing as such a high-throughput approach with a case study on the NC-Cantor alloy.

To this end, we characterize the mechanical behavior (hardness, Young's modulus and strain rate sensitivity, SRS) of the NC Cantor alloy after various annealing treatments and compare it to the behavior of CG materials. It will be demonstrated that the temperature dependent precipitation and re-dissolution of second phases can be monitored by changes in the Young's modulus of the NC-state, which can indirectly also provide qualitative information about the long-term stability of the HEAs having conventional grain sizes.

Experimental

The equiatomic HEA, CrMnFeCoNi, was synthesized by arc melting and drop-casting in pure Ar atmosphere followed by homogenization at 1200 °C for 48 hours as described elsewhere [19]. This state with grain size in the millimeter range will be referred to as cast and homogenized (CH) material. Next, the HEA was processed by high-pressure torsion (HPT) using disks 8 mm in diameter and 0.8 mm thick. The pressure during deformation was 7.8 GPa, the rotational speed was 0.2 rotations/minute, and 5 rotations were applied. In addition, material with an approximate grain size of 6 μm was analyzed (referred to as MG material here for its micrometer-sized grains), which had been fabricated by deformation processing and annealing as described elsewhere [9]. Grain sizes for the three different states are given in Table 1. These material states were separately subjected to different isochronal anneals for 1 h each at temperatures from 200 °C to 1000 °C and isothermal heat treatments at 450 °C up to 200 h.

In order to investigate the mechanical properties of these heat treated conditions, nanoindentation experiments were performed, for which the specimens were ground and polished, first mechanically with SiC paper and then mechano-chemically with colloidal silica. Nanoindentation testing was carried out in the post-annealed conditions at room temperature using a platform nanoindenter G200 (Keysight-Tec, USA) equipped with a three-sided diamond Berkovich tip. Tip shape and frame stiffness calibrations were performed at regular intervals with fused silica following the Oliver & Pharr method [25]. Depth dependent local mechanical properties were determined using a continuous stiffness measurement (CSM) unit, which measures the contact stiffness continuously by superimposing a sinusoidal load signal (45 Hz, 2 nm oscillation amplitude) on the normal indentation load. All nanoindentation experiments were performed in constant strain rate mode and at thermal drift rates of less than 0.1 nm/s. Hardness and Young's modulus (assuming a Poisson's ratio for the HEA of 0.25 [7]) were determined by constant strain rate indentation (0.05 s^{-1}) to a preset indentation depth of 2500 nm. The calculated depth

dependent mechanical properties were further averaged between 1000 nm and 1900 nm indentation depth. Local SRS data were calculated from nanoindentation strain rate jump tests [26] during which the applied strain rate was changed abruptly every 500 nm, starting at 0.05 s^{-1} , then dropping to 0.005 , followed by an increase to 0.05 , then dropping to 0.001 s^{-1} , and so on. Thermally activated processes were quantified as described elsewhere [27,28] by calculating the SRS m ($m = \partial \ln H / \partial \ln \dot{\epsilon}$) and activation volume V^* ($V^* = C^* \cdot \sqrt{3} \cdot k_B \cdot T / mH$) from the measured dependence of hardness H on strain rate $\dot{\epsilon}$ (with C^* : constraint factor of 2.8, k_B : Boltzmann constant, T : room-temperature $25 \text{ }^\circ\text{C}$).

Results & Discussion

Microstructure

The microstructural developments and the chemical decomposition of the material during annealing has been analyzed in detail (TEM, APT) and discussed in a previous paper published by Schuh et al. [19]. A short summary of the most important microstructural features is presented in Fig. 1: By applying HPT on the single-phase solid solution HEA, a NC microstructure with grain size of less than 50 nm can be achieved, as shown in the TEM micrograph in Figure 1a. In this state the single-phase solid solution character is retained, which was confirmed by APT measurements. Further annealing treatments of the NC materials led to a decomposition of the originally single-phase alloy into a state with more than one phase, including some intermetallic phases. These precipitates and new phases can be detected by advanced microscopy techniques such as TEM ([19]), by APT to probe very small volumes, see Figure 1b and by SEM (Figure 1c-e). Evidence of a newly formed crystal structure is also indicated by additional diffraction rings in TEM diffraction mode [19]. For further details and discussion the reader is referred to an earlier publication by some of the present authors (Schuh et al.[19]).

Mechanical behavior – Hardness & Young’s Modulus

After HPT, the as-deformed NC HEA has an average hardness of $6.5 \pm 0.04 \text{ GPa}$ at room temperature, which is significantly higher than the room-temperature hardness, $2.5 \pm 0.04 \text{ GPa}$, of HEA specimens that were not subjected to HPT (CH and MG states) (Figure 2). Representative load-displacement curves, hardness and Young’s modulus as well as residual impressions for NC and CH HEA are shown in Figure 2

(a: mechanical data and b. residual impressions). For both microstructural states, there is similar independence of Young's modulus on indentation depth. However, the applied load and thus the hardness is strongly influenced by the grain size, with the NC HEA showing a depth independent hardness, while the CH state is significantly influenced by indentation size effect (ISE). Focusing more on the average values and starting with the NC as-deformed condition, the hardness of the NC HEA increases further after isochronal and isothermal annealing treatments (Fig. 3a and Fig. 4, respectively). For 1 h anneals (Fig. 3a) hardness increases with annealing temperature and reaches a maximum of 7.64 ± 0.06 GPa at 500 °C. Afterwards, hardness decreases and falls to ~ 2.2 GPa for temperatures of 800 °C and higher. Heat treatments were also performed on the MG (green circles) and CH material (red triangles), both of which exhibited no hardness variation as a function of annealing temperature (Fig. 3a). The MG sample with an approximate grain size of 6 μm shows slightly higher hardness values than the CH material, which is likely related to the larger grain size of the latter (order of millimeters in comparison to several μm). For the temperature at which maximum hardness was measured after 1-hour heat treatments, additional isothermal heat treatments were conducted. The results of isothermal heat treatments at 450 °C, for times of 5 minutes to 200 h, are shown in Fig. 4. There is a significant hardness increase with annealing time, reaching a maximum of around 11 GPa after 100 h, which shows that equilibrium is not reached after 1 h at 450 °C (Fig. 3a). Beyond this maximum there is a slight decrease to 10 GPa, possibly due to grain growth. The standard deviations for these heat treatment conditions are relatively small as indicated by the small error bars. The present hardness trends agree well with the macroscopic Vickers hardness measurements performed previously by Schuh et al. [19] where the changes were correlated with the formation of metallic and intermetallic nanophases by advanced characterization techniques (TEM and APT). For short annealing times, a secondary contribution from dislocation annihilation was suggested, which is a hardening mechanism reported in NC metals [29,30].

In addition to the hardness, nanoindentation testing can be used to determine Young's modulus from the contact stiffness. The CH and MG states have Young's moduli between 205 and 220 GPa, depending mainly on the grain orientation, whereas for the initial NC state after HPT a Young's modulus of 205 ± 0.5 GPa was determined, Fig. 3b, and Fig. 4. These values for the CG, non-deformed condition are comparable to those determined for this HEA in the MG state by resonant ultrasonic spectroscopy (202 GPa,[8]). Upon annealing, the modulus of the NC material first increases to a maximum of 252 GPa at 550 °C, then remains fairly constant up to 700 °C, beyond which it decreases significantly at 800 °C and higher temperatures (Fig. 3b). Moreover, there is very pronounced scatter in the modulus within these higher-temperature annealed states as indicated by the significant error bars. Similar scatter is also

present in the Young's modulus obtained from all experiments performed on the MG and CH materials regardless of annealing temperature. Within the limits of this scatter, their moduli remain roughly constant as a function of annealing temperature. After the isothermal treatments at 450 °C (Fig. 4), the Young's modulus of the NC material increases slightly, to 262 GPa after 200 h, which indicates again the lack of equilibrium after 1 hour.

For all the above results, a significant effect of pile-up, which can influence the hardness and modulus determined using the Oliver-Pharr method [25], can be ruled out since our indentations look microscopically similar after the different heat treatments. Fig. 2b shows representative light microscopy images of indents in the CH and NC HEAs along with their mechanical data. The impressions in the CH material are affected by crystallographic orientation, showing some orientation dependent irregular pile-up formation around each indentation. In contrast, the NC HEA shows homogenous pile-up formation, but with smaller impressions overall since the maximum indentation load was reached at around 2200 nm before the pre-set indentation depth of 2500 nm was reached.

As mentioned before, the hardness increase after annealing is mainly due to precipitation hardening plus a smaller contribution from dislocation annihilation processes in the early stages. At present, these two mechanisms cannot be fully separated, however, for the hardening by annealing, which is correlated to a change in the defect structure, no change in the Young's modulus is expected. Thus, the detected changes in Young's modulus can be directly related to the formation of additional phases during annealing, since the newly formed metallic and intermetallic phases can be assumed to have higher moduli than the single-phase HEA, especially the intermetallic phases. These phases, namely, a MnNi phase, a Cr-rich phase, and a Fe-Co phase have been found in previous studies and their formation kinetics depend markedly on annealing time and temperature [19,21]) By the same token, the maximum in the modulus plot persists to higher temperatures than the maximum in hardness (Fig. 3a,b). This is because hardness is affected by three factors: the precipitation of additional nanophases, their stability as well as their average grain size. The hardness measurements on the heat-treated structure suggest that the grain size of the fcc HEA matrix increases for annealing temperatures higher than 600 °C (Fig. 3)) and for lower annealing temperatures exposed to longer times (Fig. 4: $t > 100$ h). The dissolution of the precipitates however is not directly linked to the hardness decrease as can be seen from the SEM images (Figure 1c-e). In contrast, the modulus is unaffected by grain size and therefore remains also high to higher temperatures even though hardness decreases. This implies that as long as the modulus remains high, it is a qualitative indication that additional phases are present, which is also consistent with our earlier microstructural investigations ([19], Figure 1c-e). At annealing temperatures of 800 °C and higher, the modulus drops significantly and converges to those of the CH and MG HEAs. This can be

directly correlated to a complete dissolution of the nanophases and restoration of the single phase, as shown by our previous microstructural analyses ([19] and Figure 1e). However, there is grain coarsening at elevated temperatures (see also Figure 1c-e), which leads to more pronounced scatter in the data as the tip size becomes small relative to the grain size resulting in different grain orientations being probed. A clear proof for the interrelation between phase formation in the NC state and the changes in Young's modulus can be seen in the mechanical behavior of the non-HPT samples. The different annealing treatments lead to no significant changes in the modulus (similar to what was described earlier for hardness). This is consistent with nanophase precipitation occurring only in the NC HEA and not in the MG and CH HEAs for the present set of experimental conditions and the investigated time span. Although the mechanical consequences of nanophase formation in the NC HEA can be detected even after low annealing temperatures, the continued evolution of hardness and modulus with time show that equilibrium is not reached after 1 h anneals at 450 °C (Figures 1b and 4). Nevertheless, these properties serve as useful precursor indicators of phase instabilities thereby avoiding the need for tedious microstructural analyses.

The future development of new alloys in the vast compositional space of HEAs requires experimental methods where both mechanical properties and such decomposition tendencies can be efficiently probed in a timely manner, as also Miracle et al. [22] have recently pointed out. For this purpose, the NC state has the following advantage; when the NC state is synthesized by severe plastic deformation, e.g., HPT, the alloy composition is identical to that of materials with coarser grains. However, its decomposition kinetics are significantly faster [19–21], which saves time. Furthermore, in the NC state, the larger indenter tip size compared to the microstructure results in a more representative volume being probed. By rapidly probing the phase stability of such NC HEAs it is possible to obtain results that are also relevant for coarser grained materials. As a further step and refinement of the present study the mechanical investigation of the individual newly formed phases could be envisaged. This would help to obtain a direct, quantitative correlation between measured indentation Young's modulus and the (intermetallic) phase fraction, which is however cumbersome due to the multiphase character of the alloy and beyond the scope of this paper. What we have shown here is that nanoindentation can be a powerful qualitative tool to probe decomposition tendencies as a first step, following which detailed microstructure characterization can be performed on a limited number of samples in the composition and processing conditions of interest.

Thermal activation

Besides determining the hardness and Young's modulus (as shown in Fig. 3), nanoindentation can also provide basic information on thermally activated deformation processes through characterization of SRS. Fig. 5 shows nanoindentation strain-rate jump results for the three material states considered in this study, i.e. MG, CH and NC. All the load-displacement curves are clearly affected by the strain rate changes showing some transient behavior after each abrupt strain rate change, Fig. 5a. The corresponding Young's modulus (inset in Fig. 5a), however, is not affected by the strain rate changes, exhibiting only increased scatter at lower strain rates due to the longer indentation time and thus more data points [31]. In contrast, the hardness is strongly affected by the strain rate changes, Fig. 5b. While for the CH and MG materials an indentation size effect (ISE) is found in combination with some SRS, the NC state shows pronounced SRS paired with a depth independent hardness (i.e., no ISE). Moreover, the hardness changes in the NC material occur abruptly without any pronounced transient behavior. This can be seen more clearly in Fig. 5c, which is a magnified view of one of the strain rate changes (from 0.05 s^{-1} to 0.001 s^{-1}). While the CH and MG data are dominated by an ISE in combination with a pronounced transient behavior, the NC state shows some interesting yield point phenomena. After each strain-rate jump to a lower strain rate, the hardness first drops without any pronounced transient behavior, followed by a further, unexpected small increase to an intermediate hardness maximum. Beyond that point, the hardness again decreases slightly. This indicates that the strain rate dependent hardness changes are also dependent on the grain size. Moreover, the resultant hardness changes show distinct differences among the different material states. The largest hardness change, ΔH , of 0.3 GPa occurs in the NC state, followed by the MG state (~ 0.2 GPa), with the CH condition having the smallest ΔH (0.1 GPa). To quantify this relationship between hardness difference and strain rate changes, the SRS m was calculated. The value of m increases as the grain size decreases, whereas the corresponding activation volumes show the opposite trend, see Table 1.

The nanoindentation strain rate jump experiments show that thermally activated processes are additionally influencing the overall deformation behavior of these materials. By applying simple nanoindentation methods, it was possible to probe time dependent mechanical properties of three different microstructural states with limited amount of sample volume. As expected for an NC fcc material, the higher SRS of the NC state can be explained by dislocation interactions with the grain boundaries, which has also been found in many other nanostructured fcc materials [32]. For example, the hardness change without a pronounced transient behavior paired with a distinct yield point phenomena in the NC condition was previously also reported for NC NiFe alloys in micron sized tension experiments [33]. At present, the phenomenon is still not fully understood, however it is not found in

pure NC Ni [31], suggesting that it may be related to high alloying contents. Another interesting feature is that, the CH and MG states also show some pronounced hardness changes after the strain rate jumps, which is not usually observed in pure coarse-grained or single crystalline fcc metals [26–28,32]. Generally this behavior resembles that seen in single crystal and coarse-grained bcc metals and was only once before reported for this material class [34]. In bcc crystal structure the deformation is governed by thermal activation over the Peierls stress, which leads to a pronounced SRS below a critical, material specific temperature T_c . Since both coarse grained conditions, CH and MG, show SRS values around 0.01 (0.008 (CH), 0.014 (MG)) paired with a relatively small activation volume V^* for fcc metals ($69 \cdot b^3$ (CH), $42 \cdot b^3$ (MG)), these first local results suggest a high lattice friction stress that has to be overcome by thermal activation.

By decreasing the grain size from CH to MG to NC the measured hardness differences become larger and the shape of the transient significantly changes. This might be an additional indication of an interplay between lattice resistance and thermally activated dislocation interactions with the grain boundaries.

Conclusions

The CrMnFeCoNi HEA was synthesized by high-pressure torsion as a single-phase, nanocrystalline material having the fcc crystal structure. The alloy was then subjected to various isochronal and isothermal heat treatments to decompose it into multiple metallic and intermetallic phases, as proven by advanced high-resolution microscopy techniques. Nanoindentation testing was successfully used to measure various room-temperature mechanical properties of these material states, and their properties were compared to those of coarser grained materials. The results can be summarized as follows:

- (i) Hardness and Young's modulus exhibit a similar tendency upon annealing, showing an initial increase with annealing temperature followed by a decrease at higher temperatures.
- (ii) The initial hardness increase is mainly due to the newly formed nanophases while the subsequent softening is due to grain growth and dissolution of the second phases. In contrast, the Young's modulus is not affected by grain size and is mainly dependent on the presence (or absence) of secondary phases. Therefore, nanoindentation of NC microstructures is a direct and fast way to probe the phase stability especially of single-phase HEAs and can be used as a complementary high-throughput screening approach to probe many different chemical compositions in short times. It also correlates with the long-term behavior of coarser grained materials and can therefore be used for screening purposes.
- (iii) High strain rate sensitivity was found for all tested conditions, irrespective of the grain size.

Finally, some questions still remain, e.g. for the CG states an increased fluctuation of Young's modulus suggests strong elastic anisotropy, which needs to be characterized. The high strain rate sensitivity of the coarse grained HEA is not typical of other fcc materials and the responsible mechanisms therefore need to be further studied.

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Figure 1. Advanced microscopy results of HEA after deformation by HPT and annealing, a) TEM image of as deformed, NC condition, b) APT reconstructions of 3 annealed HPT conditions at 450°C for 5 min, 1h and 15 h. and c) –e) microstructure by SEM (BSE contrast) of HPT specimens after 1 h heat treatments at 700, 750 and 800°C, respectively (intermetallic phases are indicated by circles c and d). *This figure is an adapted reproduction from Schuh et al. [19], which is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)*

Figure 2. Nanoindentation results a) mechanical data (Young's modulus, hardness and load vs displacement) for CH and NC materials after 1 h anneal at 300°C and b) corresponding light microscopy images of residual indentation arrays (circles indicate the indents whose indentation data are displayed).

Figure 3. Nanoindentation results for NC, MG, and CH materials. a) Hardness and b) Young's modulus measured at room temperature after 1 h isochronal heat treatments at different annealing temperatures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 4. Nanoindentation results for NC, MG, and CH materials. Room-temperature hardness and Young's modulus after isothermal heat treatments at 450 °C for various times. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 5. Room-temperature nanoindentation strain rate jump tests on the different material states. a) Load-displacement curves with inset showing Young's modulus vs. indentation depth. b) Hardness vs. indentation depth. c) Magnified view of hardness vs. indentation depth for strain rate jump at 1500 nm.

Table 1.

Strain rate sensitivity m and activation volume V^* ($b \sim 2.53 \text{ \AA}$).

Microstructure	m (-)	V^* ($b3$)
CH state ($d > 1 \text{ mm}$)	0.008	69
MG state ($d \sim 6 \text{ }\mu\text{m}$)	0.014	42
NC state ($d \sim 50 \text{ nm}$)	0.018	16