

Paragraph Ran in the Queries

Paper Title: Excellent strength-ductility combination in the absence of twinning in a novel single-phase VMnFeCoNi high-entropy alloy

Content :

Fundamental scientific research on high-entropy alloys (HEAs), focusing on phase stability [1,2], physical [[3], [4], [5], [6], [7]], mechanical [[8], [9], [10], [11], [12]], and functional properties [13], has increased steadily over the last two decades [13,14]. Despite this intense interest, very few single-phase equiatomic and quinary HEAs have been synthesized, e.g., the face-centered cubic (FCC) Cantor alloy (CrMnFeCoNi) [15], the body-centered cubic (BCC) Senkov alloy (TiZrNbHfTa) [16], and the hexagonal close-packed (HCP) Feuerbacher alloy (YGdTbDyHo) [17,18]. While other single-phase FCC alloys have been produced, such as the Freudenberger alloy (NiCuPdPtAu) consisting of precious metals [19,20], none have received more attention than those of the Cr-Mn-Fe-Co-Ni system, including off-equiatomic variants [21], medium-entropy subsystems [9,22], and alloys with an additional element such as Al [23]. Some of the reasons for this interest are that alloys from the Cr-Mn-Fe-Co-Ni system exhibit good formability and outstanding combinations of strength and ductility at room temperature (RT) and cryogenic temperatures [24,25].

It is now well accepted that the Cantor alloy is not thermodynamically stable as a single phase at RT, i.e., different secondary phases precipitate depending on the annealing temperature, such as a Cr-rich σ phase (space group symbol and number:

$P4_2/mnm$

, 136) at $575 < T < 800$ °C [26,27], and a combination of three secondary phases precipitate at lower temperatures: Cr-rich BCC (

$Im\bar{3}m$

, 229), Ni-Mn-rich L1₀ (

$P4/mmm$

, 123), and Fe-Co-rich B2 (

$Pm\bar{3}m$

, 221) [26]. However, the Cantor alloy does form a stable FCC solid solution above 800 °C and can be retained in this state at RT by quenching in air [8]. To critically test the concept of high-entropy alloys proposed by Yeh et al. [28], according to which a high

mixing entropy should favor the formation of a disordered solid solution, Otto and coworkers [29] investigated the stability of multiple quinary equiatomic alloys at ~1000 °C. Each of these alloys consisted of four out of the five elements of the Cr-Mn-Fe-Co-Ni system with an alternate fifth element (Ti, V, Cu, or Mo). Although the replaced elements had appropriate properties when considering the Hume-Rothery rules, meaning single-phase HEAs were expected, at least one detrimental phase precipitated in each case, mainly topologically close-packed or Laves phases. For example, Otto et al. [29] identified the precipitation of the σ phase in some alloys, which is consistent with the fact that Cr [30], V [31], and Mo [32,33] tend to stabilize this phase. Moreover, additions of Ti and/or Al to the Cantor alloy and its medium-entropy subsystems were found to stabilize the B2 phase [23,29], while Cu resulted in the formation of a second disordered FCC phase [34]. Among the equiatomic alloys studied by Otto et al. [29] (except CrMnFeCoNi), the equiatomic VMnFeCoNi alloy was the one with the lowest proportion of a secondary σ phase after annealing at 1000 °C for 72 h. Based on this observation, it was assumed in this study that VMnFeCoNi could be made single-phase FCC at higher temperatures. Therefore, the objectives here are (i) to investigate the feasibility of making this HEA single-phase FCC and (ii) to establish a processing route to obtain a model microstructure, which is essential for a reliable determination of properties. Then, we aim (iii) to determine the tensile properties and deformation mechanisms of VMnFeCoNi at RT and (iv) to compare them with those of the well-investigated Cantor alloy. Indeed, since V has a larger atomic volume than Cr, we expect greater solid solution strengthening in VMnFeCoNi and eventually different deformation mechanisms.

To address these objectives, a 2.1-kg ingot of the nominally equiatomic VMnFeCoNi alloy was induction melted from pure metals (purity ≥ 99.7 wt.%) under a partial pressure of Ar and cast in a cylindrical steel mold. The cast ingot was homogenized at 1200 °C for 48 h and then rotary swaged to a true strain of 1.8 at RT, similar to the procedure described in Ref. [35]. Pieces were cut from the swaged rod, annealed for 1 h between 1000 and 1100 °C, metallographically prepared (see Ref. [36] for details), and investigated via backscatter electron imaging (BSE) in a scanning electron microscope (SEM) of type JEOL JSM-7200F. From the microstructures shown in Fig. 1, it can be deduced that recrystallization took place with the precipitation of bright σ -phase particles (see Fig. S1 and Table S1 of the supplementary materials) for $T \leq 1050$ °C, while the equiatomic VMnFeCoNi HEA is single-phase FCC at higher temperatures. Small and dispersed black particles, identified as oxides by energy-dispersive X-ray spectroscopy (EDS, see Fig. S2 and Table S2), are also observed in Fig. 1. They presumably formed from traces of O present in the raw metals and possibly also from contamination during induction melting, similar to what is typically observed in alloys from the Cr-Mn-Fe-Co-Ni system [35,37]. More importantly, since the average distance

between oxide particles is large ($> 10\ \mu\text{m}$), they will not significantly contribute to the mechanical behavior of the alloy, i.e., an estimate of the Orowan stress is $< 2\ \text{MPa}$ [38].

An attempt was then made to establish a reference state, which should be equiatomic, single-phase FCC, with a fully recrystallized microstructure and a homogenous distribution of elements. For this purpose, the cold-worked VMnFeCoNi alloy was annealed at $1080\ ^\circ\text{C}$ (above the σ -solvus temperature) for different times, and an annealing time of 30 min was found to meet the requirements.

The alloy composition was confirmed to be approximately equiatomic by X-ray fluorescence (XRF) analysis conducted at a commercial laboratory (Revierlabor, Essen, Germany), see Table 1. Additionally, the concentrations of some impurities, as estimated via XRF, combustion infrared absorption, and carrier gas hot extraction analyses were relatively low.

Having achieved the targeted composition, the microstructure of the VMnFeCoNi HEA annealed at $1080\ ^\circ\text{C}$ for 30 min was characterized by BSE imaging, EDS, and electron backscatter diffraction (EBSD) with a metallographic cross-section perpendicular to the longitudinal axis of the swaged rod. The BSE micrograph in Fig. 2a shows a fully recrystallized microstructure with annealing twin boundaries (ATBs) [39,40]. By applying the linear intercept method to four BSE micrographs similar to that shown in Fig. 2a, the mean grain size (excluding ATBs) and the average crystallite size (accounting for ATBs) were estimated to be $59 \pm 2\ \mu\text{m}$ (statistics: ~ 700 grains) and $38 \pm 1\ \mu\text{m}$ (statistics: ~ 1100 crystallites), respectively. EDS maps taken from the same region (see Fig. 2a), using an Oxford AZtecEnergy X-MaxN detector, reveal a homogeneous distribution of the elements at the μm scale. An EBSD analysis was performed on ~ 800 crystallites using an Oxford AZtecSymmetry CMOS detector. In the inverse pole figure (IPF) map (Fig. 2b), the colors indicate the crystallographic directions that are parallel to the rod axis (see stereographic triangle at the bottom right for the interpretation of the colors), and a threshold of 15° was used to identify high-angle grain boundaries and ATBs. From the EBSD image in Fig. 2b, the linear intercept method yielded average grain and crystallite sizes of $66\ \mu\text{m}$ and $35\ \mu\text{m}$ respectively, in reasonable agreement with the values obtained from BSE images (deviations may result from the limited area scanned in EBSD). As no dominant color is apparent in the IPF map in Fig. 2b, the crystallographic orientations are randomly distributed in space. This is further quantitatively confirmed by the IPF in Fig. 2c, where the maximum pole density is 1.7 times random. Thus, the EBSD analyses confirmed that the VMnFeCoNi alloy consists of a single FCC phase and has a near-random texture

To ensure the absence of nano-scale precipitates that may have been missed by EBSD and SEM-EDS, further microstructural investigations by transmission electron microscopy (TEM) were performed. Specimens from the reference state were cut,

ground, and electrochemically thinned using a Struers TenuPol-5 (see Ref. [41] for more details), and investigated with a Tecnai Supertwin F20 G2 operating with a nominal acceleration voltage of 200 kV. The bright-field (BF) TEM micrograph in Fig. 3a1, was taken from a region close to the hole of the TEM specimen. The selected area diffraction (SAD) pattern in Fig. 3a2 was recorded from the region marked with a circle in Fig. 3a1, which shows diffraction spots that only correspond to a disordered FCC crystal structure (the region of interest contains an ATB). Additionally, TEM-EDS was employed using a Jeol-2100Plus (acceleration voltage: 200 kV) with an Oxford systems detector to confirm that no segregation had occurred at grain boundaries and that no nuclei of secondary phases had precipitated there. A scanning TEM bright-field (STEM-BF) micrograph of a region showing a triple junction of grain boundaries is displayed in Fig. 3b. The locations of the grain boundaries were confirmed with different Kikuchi patterns in the diffraction mode, and these are highlighted with white lines while the triple junction is marked with an arrow in Fig. 3b, which is also indicated on the elemental distribution maps. These reveal no distinguishable elemental segregation. Based on the results shown in Fig. 2, Fig. 3, it is now concluded that the recrystallized VMnFeCoNi alloy is chemically homogeneous, nearly untextured, and single-phase FCC.

In the case of the equiatomic CrMnFeCoNi HEA and associated medium-entropy subsets, it has been suggested that Cr causes the most significant lattice distortion [42,43] and thus makes the largest contribution to solid solution strengthening [44,45]. Considering that V has a larger atomic volume than Cr [46,47], the substitution of Cr in CrMnFeCoNi by V to give VMnFeCoNi is expected to lead to stronger lattice distortions and thus a larger solid solution strengthening effect. To investigate this possibility, the RT-tensile behavior of the VMnFeCoNi HEA in the reference state was studied. For this purpose, flat dog-bone-shaped specimens (gauge section dimensions: 20 mm \times 1.2 mm \times 4 mm) were tested at a nominal strain rate of $\sim 10^{-3}$ s $^{-1}$. The engineering stress-strain curves in Fig. 4a reveal an impressive strength-ductility combination for an FCC solid solution, i.e., the VMnFeCoNi HEA (red curves) has a yield stress, ultimate tensile strength (UTS) and ductility of ~ 250 MPa, ~ 675 MPa, and ~ 60 %, respectively. To investigate how the substitution of Cr by V affects the mechanical behavior of the VMnFeCoNi HEA, its tensile curves are compared to those of the Cantor alloy (black curves) with a similar grain size (60 μ m, see Ref. [48]) in Fig. 4. For both alloys, the solid and dashed lines correspond to different specimens, tested to investigate reproducibility. Interestingly, the yield stress of VMnFeCoNi (~ 250 MPa) is much higher than that of CrMnFeCoNi (~ 190 MPa). This is likely because V in VMnFeCoNi has a larger volume misfit than Cr in the Cantor alloy, resulting in greater solid solution hardening, analogous to the improvement in yield stress in VCoNi compared to CrCoNi [49]. However, further work, beyond the scope of this paper, is needed to confirm this hypothesis.

VMnFeCoNi is additionally found to have a far better strength-ductility combination than the Cantor alloy. To identify the reason for this difference, the work hardening rate (WHR) is shown as a function of true stress in Fig. 4b. Here, the WHR of CrMnFeCoNi (black curve) is found to decrease rapidly in the initial stages from 5 to 2 GPa (true stress < 300 MPa), as the number of grains participating in the plastic deformation gradually increases [50]. After a very short plateau (300 MPa < true stress < 500 MPa), the WHR decreases at a nearly constant rate presumably due to the generalization of cross-slip [51]. In contrast, after an initial sharp drop in WHR, VMnFeCoNi shows a high and more sustained WHR (red curves in Fig. 4b). Since the Considère criterion [38] is fulfilled in both alloys (i.e., necking instability begins when the WHR becomes equal to the true applied stress [38]), the superior WHR of VMnFeCoNi allows postponing necking instability and results in a better strength-ductility combination.

Stable and high WHRs are usually attributed to twinning-/transformation-induced plasticity (TWIP/TRIP) in alloys of the Cr-Mn-Fe-Co-Ni system [9,22,52]. To identify whether these contribute to the superior work-hardening capability of VMnFeCoNi compared to CrMnFeCoNi, TEM investigations were performed on specimens strained at RT to ~10%, ~25%, and fracture (see tensile curves in Fig. S3). The BF-TEM micrographs in Fig. 5 show linear features. To determine their nature, an SAD pattern was taken for each state (see insets), which revealed no signs of deformation twinning or martensitic transformation. This conclusion was also confirmed by examination of six grains from two TEM samples taken from a fractured specimen, far away from the region affected by strain localization. The absence of deformation twins (and martensite variants) in VMnFeCoNi implies that its stacking fault energy is relatively high at RT, similar to what has been reported for the equiatomic VCoNi medium-entropy alloy [49,53]. Moreover, the microstructural evolution in Fig. 5 indicates that the sustained WHR in VMnFeCoNi (Fig. 4b) is related to dislocation interactions. For instance, the transition from single slip to multiple slip in a significant fraction of the grains (similar to the transition between stage I and stage II in single crystals) could be the reason for the abrupt change in the WHR-versus-stress curve at ~350 MPa in Fig. 4b. This behavior is known to be stronger when the grain size is large and dislocation slip is particularly planar (see [41] for more details), which is the case in VMnFeCoNi as discussed below.

Fig. 5

In Fig. 5, the traces of {111} planes, marked with red dashed lines, are parallel to the linear features (maximum deviation: 5°) and can thus be identified as slip bands,

characteristic of planar slip [54,55]. With increasing strain, the distance between slip bands in VMnFeCoNi is progressively reduced (Figs. 5a-c). As they act as barriers to dislocation motion, the dislocation mean free path decreases with increasing deformation, leading to the WHR plateau in Fig. 4b. In contrast, dislocation slip in CrMnFeCoNi tested under similar conditions is more "wavy" [24,41], with dislocation cells forming at large deformations, resulting in lower WHRs (Fig. 4b).

To summarize, when Cr in CrMnFeCoNi is replaced by a larger solute such as V to give VMnFeCoNi, the yield strength increases and dislocation slip becomes more planar (despite the increase in SFE), resulting in a superior work-hardening capability. These trends are similar to those reported in binary solid solutions (e.g., Si-addition to Ni [56]), austenitic steels (Mn-addition to steels [55]), and HEAs (Ti+Al-addition to Ni₂CoCrFe [54]), where TWIP/TRIP effects are absent, but solute additions promote planar slip with the formation of intersecting slip bands. The wavy-to-planar slip transition is usually associated with (i) an increase in the degree of short-range ordering (SRO) or a decrease in cross-slip propensity due to (ii) a decrease in SFE or (iii) solute-Shockley partial interactions [57], all of which prevent the constriction of the Shockley partials into a perfect dislocation [58,59]. In the present work, since the SFE of VMnFeCoNi (> 100 mJ/m² estimated based on Ref. [60]) is larger than that of CrMnFeCoNi (~ 35 mJ/m² [3]), we can conclude that planar slip in VMnFeCoNi and its excellent work-hardening behavior may be related to either the presence of SRO, solute-Shockley interactions or a combination of both. Further work, beyond the scope of the present study, is required to clarify these aspects.