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A TRIP-assisted dual-phase high-entropy alloy: Grain size and phase fraction effects on deformation behavior

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ABSTRACT

We present a systematic microstructure oriented mechanical property investigation for a newly developed class of transformation-induced plasticity-assisted dual-phase high-entropy alloys (TRIP-DP-HEAs) with varying grain sizes and phase fractions. The DP-HEAs in both, as-homogenized and recrystallized states consist of a face-centered cubic (FCC) matrix containing a high-density of stacking faults and a laminate hexagonal close-packed (HCP) phase. No elemental segregation was observed in grain interiors or at interfaces even down to near-atomic resolution, as confirmed by energy-dispersive X-ray spectroscopy and atom probe tomography. The strength-ductility combinations of the recrystallized DP-HEAs ($Fe_{50}Mn_{30}Co_{10}Cr_{10}$) with varying FCC grain sizes and HCP phase fractions prior to deformation are superior to those of the recrystallized equiatomic single-phase Cantor reference HEA ($Fe_{20}Mn_{20}Ni_{20}Co_{20}Cr_{20}$). The multiple deformation micro-mechanisms (including strain-induced transformation from FCC to HCP phase) and dynamic strain partitioning behavior among the two phases are revealed in detail. Both, strength and ductility of the DP-HEAs increase with decreasing the average FCC matrix grain size and increasing the HCP phase fraction prior to loading (in the range of 10–35%) due to the resulting enhanced stability of the FCC matrix. These insights are used to project some future directions for designing advanced TRIP-HEAs through the adjustment of the matrix phase's stability by alloy tuning and grain size effects.

1. Introduction

High-entropy alloys (HEAs), also known as multi-principal element materials or compositionally complex compounds, have drawn significant attention during the last decade [1–9]. In 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 were that phase separation would lead to the formation of brittle intermetallic compounds or that partitioned alloying elements would reduce the targeted solid solution hardening effect [10]. In this context, several alloys have been proposed that develop single-phase face-centered cubic (FCC; e.g., FeMnNiCoCr [3,5] and $FeNiCoCrAl_{0.3}$ [11]), body-centered cubic (bcc; e.g., TaNbHfZrTi [12], VNbMoTaW [13], and HfMoTaTiZr [14]) and hexagonal close-packed (HCP; e.g., HoDyYGdTb [15]) crystal structures. Among these, the FeMnNiCoCr system, a typical single FCC phase solid solution HEA at room temperature that can be produced by conventional casting, has particularly excellent mechanical properties [2,16,17], including exceptional cryogenic fracture toughness [5].

However, a number of studies revealed that entropy-stabilized single-phase HEAs are often hard to realize and are also not necessarily equipped with superior properties [3,4,16,18–20]. These observations have encouraged efforts to relax the strict restrictions on HEA design regarding single-phase stability. Motivated by this, we recently developed a new class of HEAs, namely, transformation-induced plasticity-assisted dual-phase (TRIP-DP) HEA [1]. The two high-entropy phases present in this TRIP-DP-HEA (i.e., FCC γ matrix and HCP ε phases) are compositionally equivalent [1]. The new alloy design concept was realized in the four-component FeMnCoCr HEA system. The new material combines the solid-solution strengthening effect inherent in HEAs with the

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TRIP effect known from certain high strength steels [21–25], resulting in improved strength and ductility compared to the above mentioned single-phase HEAs [1,2,5]. In the new TRIP-DP-HEAs, the micro-composite effect associated with its dual-phase microstructure and the displacive phase transformation upon deformation play key roles in enhancing the strain hardening potential of the material and hence its strength and ductility. The deformation-stimulated transformation behavior is influenced by the thermodynamic stability of the FCC matrix phase [1], which in turn is related to the initial FCC grain size, the alloy content and elemental partitioning, the HCP phase fraction present in the matrix prior to deformation and the load partitioning among the two phases.

We observed before that grain-refinement leads to substantial improvement in both strength and ductility in these materials [1], however, the underlying mechanisms enabling such behavior were not investigated. Here, we thus address these questions including the influence of the FCC grain size on the HCP phase fraction prior to loading, the effect of the initially available HCP phase fraction on the overall deformation response and kinetics, and the influence of the FCC grain size on its phase stability. For these reasons we produced DP-HEAs with varying FCC grain sizes and initially available HCP phase fractions by corresponding thermal and grain refinement processing. In the following we present these microstructures and the associated microstructure-mechanical property relations.

2. Methodology

2.1. Alloys processing

The DP-HEA was first cast in a vacuum induction furnace using pure metals (>99.8 wt. % pure) to a predetermined composition of 50Fe-30Mn-10Co-10Cr (at. %). The as-cast ingot ($10 \times 50 \times 150\ mm^3$) was hot-rolled at 900 °C to a thickness reduction of 50%. Subsequently, the alloy sheets of 5 mm thickness were homogenized at 1200 °C for 2 h in Ar atmosphere followed by water-quenching. The exact composition (including the contents of residual elements) of the homogenized alloy was obtained by conducting a comprehensive chemical analysis and the results are listed in Table 1. The grain size of the homogenized alloy sample is nearly the largest value currently we can obtain in the alloy sample without observable chemical inhomogeneity based on the fact that the sample was heat-treated at high temperature (1200 °C) for a long time (2 h). In order to obtain samples with various grain sizes and phase fractions, the homogenized alloy was cold-rolled to a thickness reduction of 60% (thickness changed from 5 to 2 mm) and subsequently annealed at a furnace temperature of 900 °C in Ar atmosphere for 3, 5, 10, 15, 30 and 60 min, respectively, followed by water-quenching. Note that for the 3 min annealing, the true temperature that the sample actually reached might be lower than the furnace temperature (900 °C) due to the short annealing time. The short annealing time (3 min) was used to obtain nearly the smallest grain size value in a fully recrystallized alloy sample, and hence to ensure that we investigated the possible large range of grain sizes currently we could obtain in this new alloy.

Table 1
Composition (including the contents of possible residual elements) of the homogenized TRIP-DP-HEA (wt. %).

Elements	Fe	Mn	Co	Cr	Cu	Ni	Mo
	Bal.	28.5	11.1	9.77	0.333	0.0114	<0.002
Elements	Sb	Sn	C	N	O	P	S
	<0.001	<0.01	0.0064	0.0077	0.025	<0.001	0.0063

2.2. Analysis

The microstructures of the alloys were analyzed using multiple techniques. Electron backscatter diffraction (EBSD) measurements were carried out using a Zeiss-Crossbeam XB 1540 FIB scanning electron microscope (SEM) with a Hikari camera and the TSL OIM data collection software. Back-scattered electron imaging (BSEI) and electron channeling contrast imaging (ECCI) analyses [26] were performed in a Zeiss-Merlin instrument. The elemental distribution in the grain-refined TRIP-DP-HEA samples was investigated using energy-dispersive X-ray spectroscopy (EDS) and atom probe tomography (APT) (LEAP 3000X HR, Cameca Inc.). Site-specific lift-out of APT tips was performed from the regions including phase and grain boundaries (revealed by a prior EBSD scan) using the focused ion beam (FIB) technique (FEI Helios Nanolab 600i) [27–29].

Rectangular dog-bone-shaped tensile specimens, with a thickness of 1 mm, were sectioned from the alloys by electrical discharge machining (EDM). The gage length and width of the tensile specimens were 10 and 2.5 mm, respectively. Uniaxial tensile tests were carried out at ambient temperature using a Kammrath & Weiss tensile stage at an initial strain rate of $1 \times 10^{-3}\ s^{-1}$. To confirm reproducibility, three tensile specimens for each alloy were tensile tested. The evolution of local strain during tensile testing was determined by digital image correlation (DIC) method using Aramis system (GOM GmbH) [30–32].

The deformation mechanisms in the DP-HEAs were investigated by EBSD and ECCI at different regions of the fractured tensile samples with different local strain levels [33–35]. XRD measurements were performed on different regions of the tensile samples using the X-ray equipment ISO-DEBYEFLEX 3003 in conjunction with Co $K_{\alpha 1}$ ($\lambda = 1.788965$ Å) radiation operating at 40 kV and 30 mA between 40 and 130 deg (2θ) at a step size ($\Delta 2\theta$) of 0.05 deg and a counting time of 20 s per step. The X-ray beam shape was in point focus with a beam size of 1.5 mm. Phase fractions were also obtained by Rietveld analysis of XRD patterns using the software MAUD (version 2.53).

Prior to the above EBSD, ECCI and XRD measurements, the sample surfaces were first ground using silicon carbide paper from 600 to 4000 granulation, followed by polishing with 3 and 1 μm diamond suspensions. Fine polishing was performed using an oxide suspension (OPS) with silica particle size around 50 nm for more than half an hour to effectively remove the deformation layer caused by mechanical grinding. The sample surfaces were finally polished with ethanol to remove the nano-silica particles.

3. Results

3.1. Microstructure prior to deformation

3.1.1. Microstructure in the as-homogenized coarse-grained (CG) dual-phase HEA

Fig. 1 shows a typical analysis of the microstructure of the homogenized CG DP-HEA. Fig. 1a–c gives the BSE, ECCI and EBSD images. These data reveals that the alloy consists of two phases, namely, FCC γ matrix and HCP ε phase. The HCP ε phase is formed within the FCC γ matrix and mainly exhibits laminate morphology. According to the calculation from multiple BSE images and EBSD maps, the γ matrix has an average grain size of approximately 45 μm while the thickness of the ε laminate is varying between the submicron scale to more than 10 μm. From EBSD analysis, the average fractions of the FCC γ and HCP ε phases are approximately 72% and 28%, respectively. High angle grain boundaries (HAGBs, misorientation greater than 15°) prevail in the homogenized alloy. They occupy a fraction of more than 80%, while the fraction of low