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Fcc nanostructured TiFeCoNi alloy with multi-scale grains and enhanced plasticity

Zhiqiang Fu [a,b,*], Benjamin E. MacDonald [a], Dalong Zhang [a], Bingyong Wu [b], Weiping Chen [b], Julia Ivanisenko [c], Horst Hahn [c], Enrique J. Lavernia [a,**]

[a] Department of Chemical Engineering and Materials Science, University of California, Irvine, CA 92697, USA
[b] Guangdong Key Laboratory for Advanced Metallic Materials Processing, South China University of Technology, Guangzhou, Guangdong 510640, China
[c] Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), D-76021 Karlsruhe, Germany

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ABSTRACT

Face-centered cubic (fcc) nanostructured high entropy alloys (HEAs) are characterized by high strength and low plasticity. The objective of the present study was to investigate the question of whether it is possible to increase plasticity while retaining strength in a medium-entropy TiFeCoNi alloy by promoting the formation of a multi-scale microstructure. To accomplish this objective we synthesized a bulk $Ti_{10}Fe_{30}Co_{30}Ni_{30}$ medium-entropy alloy (MEA) via mechanical alloying (MA) and spark plasma sintering (SPS). This synthesis approach yielded a multi-scale microstructure consisting of distinctly coarse grains (>1 μm) and nanosized grains. The mechanisms responsible for the associated mechanical behavior are discussed.

Despite possessing multiple principal elements, the recently emerged medium-entropy alloys (MEAs) and high-entropy alloys (HEAs) can readily form solution-like phases instead of ordered intermetallic phases, and accordingly have attracted attention for two primary reasons. First, MEAs and HEAs provide a novel alloy design framework that, in principle, can be used to attain combinations of physical and mechanical properties heretofore unattainable with conventional alloys [1]. Second, available data reports of strength and other mechanical properties suggest notable enhancements in performance that exceed those of conventional metals and alloys [2–4]. The published literature reveals that MEAs and HEAs with a face-centered cubic (fcc) structure display exceptional fracture toughness and outstanding ductility from room-temperature to cryogenic temperatures [5,6]. However, published data also reveals that fcc structured MEAs and HEAs exhibit low yield strength (≤500 MPa) at room temperature, which will hinder their use in many structural applications [3,5–7]. This behavior has been attributed to the fact that the so-called: "severe lattice distortion" that is characteristic of HEAs and MEAs and which can impede dislocation glide and thereby lead to strengthening, has been found to be absent in single-phase fcc HEAs [8].

In view of the above findings, recent studies report that a number of approaches have been proposed to enhance the room-temperature yield strength of fcc structured MEAs and HEAs, including: twinning-induced ductility [5], introducing phase transformation-induced ductility [9,10], incorporating precipitates [11], interstitial alloying [12], and grain size refinement [13]. Some of these strategies have been shown to attain limited enhancement in yield strength; for example the yield strength increased from 159 MPa to 355 MPa with the addition of 1.1 at.% carbon to a $Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr_6$ HEA matrix [12]. Typically, reducing grain size down to the nanoscale in conventional alloys can effectively increase yield strength, but this increase is also coupled with a drastic decrease in the plasticity due to constrained dislocation activity [14]. The same phenomenon is also observed in fcc structured HEAs [13]. In the case of nanostructured metals and alloys, the introduction of multi-scale grains as a strategy to achieve balanced strength and ductility has shown some promise [15,16] and recent preliminary reports for fcc structured HEAs are notable [13].

The combination of mechanical alloying (MA) and spark plasma sintering (SPS) represents a viable approach to fabricate bulk nanostructured alloys with a multi-scale microstructure, partly due to the fact that SPS is a field assisted sintering technique, which can deliver high heating rates and hence high local temperature gradients [17]. However, in SPS processed fcc nanostructured HEAs comprised of five or more principal elements, most of the coarse grains (CG) reportedly remain under 1 μm that has been attributed to the "sluggish diffusion" effect associated with the large variation in the local lattice potential energy associated with multi-component elements [2,3,13,18]. In view of this limitation, we designed a quaternary medium-entropy TiFeCoNi

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* Correspondence to: Z. Fu, Department of Chemical Engineering and Materials Science, University of California, Irvine, CA 92697, USA. ** Corresponding author.
E-mail addresses: zhiqianf@uci.edu (Z. Fu), lavernia@uci.edu (E.J. Lavernia).

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alloy with an FCC structure to degrade the high-entropy“sluggish kinetics” effect in order to facilitate the formation of a multi-scale microstructure comprised of coarse grains (>1 μm) and nanosized grains.

Thus, in view of the above discussion, this letter was motivated by the question of whether it is possible to design and fabricate fcc structured MEAs with enhanced plasticity. To accomplish this objective, a medium-entropy $Ti_{10}Fe_{30}Co_{30}Ni_{30}$ (at.%) alloy was designed based on the single-phase fcc equi-atomic FeCoNi MEA matrix with the addition of 10 at.% Ti, with parameters (Ω, δ and *VEC*) that fit the empirical conditions which can potentially form single fcc solid-solution phase [19, 20]. In addition, the generation of multi-scale grains in this medium-entropy $Ti_{10}Fe_{30}Co_{30}Ni_{30}$ alloy was accomplished via MA and SPS. Finally, the microstructure, phase compositions and mechanical behavior were systematically investigated.

Elemental powders of Ti, Fe, Co and Ni with high purity (>99.7 wt%), possessing average particle sizes of 45 μm, were used as starting materials for generating the bulk $Ti_{10}Fe_{30}Co_{30}Ni_{30}$ (at.%) alloy. The as-received Ti, Fe, Co and Ni elemental powders were blended for 4 h. Tungsten carbide milling media and the blended powders were then placed in stainless-steel vials filled with argon gas in a ball-to-powder weight ratio of 10:1. The entire MA process was carried out in a high energy planetary ball mill at a rotation speed of 300 rpm for 40 h of wet milling, using cyclohexane as the process control agent (PCA) to prevent powder agglomeration. Following the MA process, the 40 h wet milled powders were placed in a vacuum drying chamber at 70 °C with the aim to evaporate cyclohexane. The dried powders were then allowed to pass through a −200 mesh (≤75 μm) sieve. A Dr. Sinter 825 apparatus (Sumitomo Coal Mining Co. Ltd., Japan) was utilized to consolidate the sieved powders at 1273 K with a heating rate of 100 K min^{-1} and a holding time of 8 min. During the process, the vacuum pressure was maintained <8 Pa and a constant pressure of 30 MPa were consistently applied during consolidation. This SPS process produced samples with a geometry of Ø20 mm × 10 mm.

Transmission electron microscopy (TEM) studies were carried out using an FEI CM-20 (200 kV) or a JEOL JEM-2500SE (200 kV) with selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS). A FEI Quanta 3D scanning electron microscopy (SEM) equipped with EDS was used to study the microstructures and chemical compositions of the as-milled powders and bulk samples, as well as the fracture morphology of bulk samples. A Bruker D8 ADVANCE X-ray diffractometer with a Cu $K\alpha$ radiation was utilized to identify the phase composition of milled powders and bulk samples. From the SPS sintered samples, the specimens for SEM observation were first prepared by polishing, followed by etching with a dilute aqua regia solution. Thin foil specimens for TEM observation were prepared via polishing using SiC grit papers followed by Ion milling. Compression tests at ambient temperature for the bulk samples with the geometry of Ø3 mm × 4.5 mm was performed on an Instron 5500 testing system at a strain rate of 1×10^{-3} s^{-1}.

Fig. 1(a) shows three XRD patterns of the $Ti_{10}Fe_{30}Co_{30}Ni_{30}$ powders before and after milling as well as the SPS sintered compacts. As expected, all four of the constituent elements are identified in the blended powders (0 h). As the milling time increases to 40 h, a single fcc structured solid-solution phase can been observed. However, following SPS, the sintered bulk samples are comprised of a primary fcc structured phase with a small amount of unindexed phases. The unindexed phases are likely a complex mixture of oxides and carbides, which are reportedly formed during either the MA process or the SPS process [21]. Further studies are needed to understand the unindexed phases and their formation mechanisms. The absence of these peaks in the as-milled powder pattern is attributed to the small volume fraction of the phase along with the peak broadening due to the nanocrystalline nature of the powder, which leads to the diffraction peaks being overwhelmed by the XRD background [21]. Furthermore, the peaks of the sintered bulk samples are significantly narrower than those of the 40 h as-milled powders due to grain growth during the SPS process [13,22]. Fig. 1(b) shows the morphology and qualitative size distribution of the 40 h as-milled powder particles, including the corresponding EDS mapping of Ti, Fe, Co, Ni. The 40 h as-milled powders exhibit near-equiaxed and irregular morphology, with particle sizes varying from several microns to 30 μm. It is worth noting that the circled areas in the SEM image of Fig. 1(b) correspond to the dark areas of EDS mapping of Ti, Fe, Co, Ni elements, which are caused by a height fluctuation in the powders associated with significant differences of particle size, and their non-planar surfaces. In other words, the constituent Ti, Fe, Co and Ni elements are uniformly distributed except in these dark areas. The semi-quantitative EDS/SEM results of the chemical distribution of the elemental constituents; Ti, Fe, Co and Ni are ~10.2, 29.6, 30.0 and 30.2 at.%, respectively, suggest that the chemical composition of the 40 h as-milled powders is relatively close to the target nominal composition ($Ti_{10}Fe_{30}Co_{30}Ni_{30}$). Additionally, cross-sectional studies of high-magnification SEM image and EDS mapping of 40 h as-milled powders also show that Ti, Fe, Co and Ni elements are uniformly distributed (See Supplementary Fig. 1). Note that EDS analyses in Supplementary Fig. 2 also reveal that the chemical composition of the 40 h as-milled powders is remarkably similar to the target nominal composition. Furthermore, bright-field TEM image of 40 h as-milled powders and its corresponding SAED pattern in Supplementary Fig. 3 confirms the presence of single fcc structure. Therefore, we note that a single fcc solid-solution phase was formed following 40 h of MA.

An SEM image of the bulk $Ti_{10}Fe_{30}Co_{30}Ni_{30}$ MEA following SPS is shown in Fig. 2. Evidently, the microstructure is composed of two distinctive regions: dark regions, marked region 1 in Fig. 2, that correspond to coarse grains and light gray regions, marked region 2 in Fig. 2, that

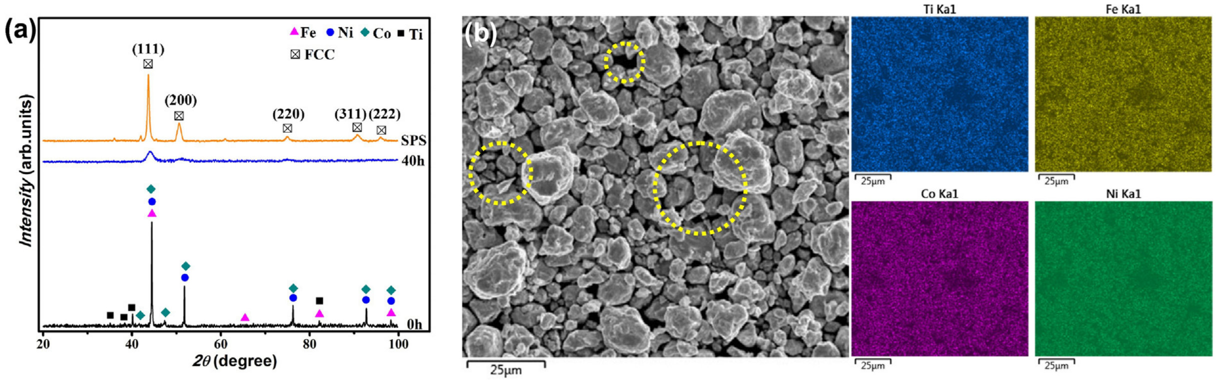

Fig. 1. (a) XRD patterns of $Ti_{10}Fe_{30}Co_{30}Ni_{30}$ powders and bulk samples, (b) Representative SEM image of the 40 h as-milled $Ti_{10}Fe_{30}Co_{30}Ni_{30}$ powders, and corresponding EDS mapping of Ti, Fe, Co, Ni, showing they are uniformly distributed.