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A novel, single phase, non-equiatomic FeMnNiCoCr high-entropy alloy with exceptional phase stability and tensile ductility

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A non-equiatomic FeMnNiCoCr alloy is introduced and characterized at multiple scales employing various characterization techniques (e.g. atom probe tomography, electron channeling contrast imaging, electron backscatter diffraction, etc.) to elucidate (i) the role of configurational entropy and (ii) the intrinsic tensile ductility of high-entropy alloys. Results reveal that the new material is a true high-entropy alloy with a stable random solid solution despite its comparably low configurational entropy, and that it has excellent tensile ductility irrespective of the substantial lattice distortion.

Keywords: Non-equiatomic; High-entropy alloy; Atom probe tomography; Ductility; ECCI

High-entropy alloys (HEAs) are multi-component systems based on the novel alloy design strategy of configurational entropy (CE) maximization. This strategy aims at a reduction of Gibbs free energy by the increase in CE [1], to design phases with simple structures, rather than brittle ordered intermetallics typical of many multi-component systems [2–4]. As a result of multiple alloy components creating strong lattice distortion, HEAs are promising candidates for many potential applications with expectedly high solid-solution strengthening and excellent resistance to high-temperature softening [2,3,5].

To this end, HEAs were initially defined to consist of at least five principal elements of concentrations between 5 and 35 at.%, in order to maximize the CE and facilitate the formation of solid solutions. Recent reports, however, have questioned such a dominant role of the CE independent of the mixing enthalpy, and have stressed that the Gibbs free energy is decisive for phase formation, even in cases of increased CE [6,7]. While the role of the CE is still under debate, it is interesting to note that the majority of the introduced HEAs still follow the original concentration design criterion, i.e. near-equiatomic ratios, while non-equiatomic HEAs have rarely been investigated.

On the other hand, although many HEAs have been designed and studied recently, their tensile test performance was rarely documented [8–13]. Instead, mechanical properties were often characterized in terms of compression tests or hardness. In fact, with the exception of a very recent work reporting good ductility [13], most of the HEAs designed to date have very limited tensile ductility, often not exceeding a few percent of strain prior to fracture. In this context it appears essential to better understand whether the limited ductility is arising from processing issues (e.g. due to consolidation problems during mechanical alloying), characterization issues (e.g. due to undetected intermetallic phase formation[1]) or due to any unknown intrinsic limitations of such multi-component systems with strong solid-solution hardening.

This study aims at improving our understanding on these points, namely: (i) the role of CE in the phase formation, and (ii) the true tensile behavior of HEAs. For this purpose we introduce a novel $Fe_{40}Mn_{27}Ni_{26}Co_5Cr_2$ (at.%) HEA, which offers several advantages in the context mentioned above: its CE (i.e. 10.8 J K^{-1} mol^{-1}, equal to ~130% of gas constant, R) is higher than the fusion entropy of most metals (i.e. ~R), and hence fits well into the HEA definition. Its CE is, however, ~20% lower compared to that of a recently suggested equiatomic FeMnNiCoCr HEA [4,7,13]. This difference enables us to study the role of the entropy component on the stability and tensile

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[1] X-ray diffraction, the standard technique employed in HEA characterization, is not fully reliable in detecting sub-micron intermetallic phases [6,19], requiring atom probe tomography measurements for full structural analysis.

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behavior of HEAs. Also, the effects of consolidation issues or brittle intermetallic phases are ruled out through liquid-metallurgical processing and characterization down to the atomic scale, allowing assessment of the intrinsic tensile ductility of the designed material.

The alloy was melted from pure metals (purity > 99.8 wt.%) in a vacuum induction furnace, cast into a water-cooled copper mold and furnace-cooled. Following hot-rolling to 50% thickness reduction at 900 °C, it was homogenized at 1200 °C for 2 h in Ar atmosphere, and quenched in water. Further grain refinement was achieved through cold-rolling to 64% thickness reduction and subsequent 900 °C annealing in Ar atmosphere for 10 min.

The characterization of phase formation and thermal stability was carried out by X-ray diffraction (XRD) and differential scanning calorimetry (DSC), respectively. During XRD, specimens were mounted on a Huber-2 goniometer and exposed to Co K_α radiation ($\lambda = 1.79$ Å). The Metero0D detector swept a 2θ range from 0° to 120° with a step size of $\Delta 2\theta = 0.05°$. DSC experiments were performed in a SETARAM Setsys 16/18 device between 20 °C and 1300 °C at different rates (5–10 K min^{-1}) in Ar atmosphere.

Microstructure characterization was carried out on as-cast, hot-rolled, homogenized, cold-rolled and recrystallized samples. Here we focus on the homogenized state. Secondary electron (SE) imaging, energy-dispersive X-ray spectroscopy (EDX) and electron backscatter diffraction (EBSD) were conducted in a 6500F JEOL field emission gun-scanning electron microscope (FEG-SEM) equipped with an EDAX software and a TSL OIM EBSD system. Elemental distribution at atomic scale was studied using a local electrode atom probe tomography (APT) (LEAP 3000X HR, Cameca Inc.). Tip specimens for APT were prepared in a FEI Helios Nanolab 600i dual-beam focused ion beam (FIB) device as described in Ref. [14]. To verify the chemical homogeneity in the vicinity of grain boundaries (most favorable positions for intermetallics [6]), two tips were lifted out from areas adjacent to a grain boundary, one from a (<001>//ND) oriented grain and the other from a (<111>//ND) oriented grain.

Mechanical properties of homogenized, cold-rolled and recrystallized states were evaluated at room temperature, with a strain rate of 2.5×10^{-3} s^{-1} using a Kammrath & Weiss stage and dog-bone-shaped specimens of gauge geometry of 4 mm × 2 mm × 1 mm. For trace analysis, samples with a gauge geometry of 10 mm × 7 mm × 1 mm were deformed to 3%, 13% and 28% strain. Prior to tensile deformation, one surface of these samples was polished for trace analysis, while a speckle pattern was applied to the other surface for digital image correlation analysis (Aramis, GOM GmbH) [15,16].

To reveal the deformation mechanisms, microstructures of homogenized samples were investigated after the tests using multi-focus imaging with a Leica DM 4000M optical microscope (OM) for trace analysis, and quantitative electron channeling contrast imaging (ECCI) [17] in a FEG/FIB dual-beam Zeiss-crossbeam XB1560 FIB-SEM, for the evolution of the dislocation structures.

First, XRD and DSC results of the as-cast and homogenized states are presented (Fig. 1). Both XRD patterns show only single-phase face-centered cubic (fcc) peaks (lattice parameter = 3.60 Å), indicating a single-phase

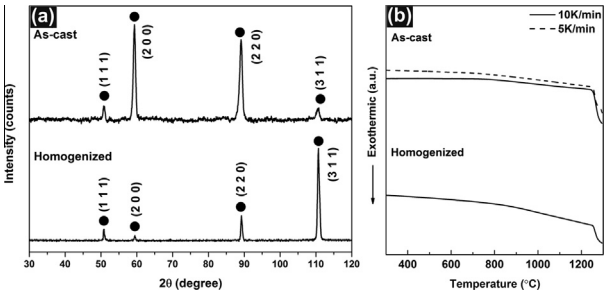

Figure 1. (a) XRD patterns and (b) DSC heating curves of as-cast and homogenized states.

solid solution in both states. DSC heating curves obtained at a low heating rate of 5 K min^{-1} reveal no exothermic or endothermic phase transformation peaks up to melting point (~1250 °C). These data show that the material consists of a very stable fcc phase.

Figure 2a and b shows the homogenized alloy in fully recrystallized state with equiaxed grains containing annealing twins. The EBSD scan at the same area (1 μm step size) (Fig. 2c) and high-resolution EBSD measurements (100 nm step size) (Fig. 2d) confirm the presence of a single fcc phase. Unindexed points arise from 0.6 vol.% porosity.

For mapping the compositional homogeneity, EDX maps of the same area in Figure 2b and c are presented (Fig. 2e). All elements are homogeneously distributed, except for some minor inhomogeneity due to the formation of manganese oxides, which is a typical processing effect in high Mn alloys [7,12]. For studying chemical homogeneity at atomic scale, APT measurements were carried out: no segregation or enrichment was observed in the analyzed volumes of 98 × 97 × 117 nm^3 and 90 × 90 × 141 nm^3 of representative concentrations $Fe_{40.3}Mn_{26.0}Ni_{25.6}Co_{6.1}Cr_{2.0}$ and $Fe_{40.8}Mn_{27.1}Ni_{24.1}Co_{5.7}Cr_{2.3}$ (Fig. 2f and g), respectively. One-dimensional concentration–depth profiles of all elements are plotted along a cylindrical region of interest with a diameter of 10 nm through the analyzed volume, revealing no statistically significant concentration fluctuations (Fig. 2f_2 and g_2). The statistics of the elemental distribution are further quantified by a binomial analysis. The frequency distribution of the elemental concentrations in both analyzed volume portions matches the reference binomial random distributions very well (Fig. 2f_3 and g_3). The relative deviation from randomness is evaluated in terms of several parameters, as listed in the inset table. μ, as a normalized auto-correlation parameter of χ^2, can assume values between 0 and 1, where 0 represents randomness and 1 represents complete association with solutes of the same type [18]. In the two analyzed tips, all elements show μ values close to 0, i.e. practically complete randomness. All these analyses give proof of a random single fcc solid solution, confirmed down to atomic scale.

These results enable us to come back to the first discussion point mentioned above, namely to the role of CE on phase formation in multi-component alloys. Despite its significantly lower CE compared to the equiatomic FeMnNiCoCr system [7], the introduced non-equiatomic HEA consists of a very stable single phase solution up to the melting point. This result supports previous work, where the formation of multiple phases