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Controlled formation of coherent cuboidal nanoprecipitates in body-centered cubic high-entropy alloys based on $Al_2(Ni,Co,Fe,Cr)_{14}$ compositions

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ABSTRACT

Microstructures and mechanical properties of Al-Ni-Co-Fe-Cr high-entropy alloys (HEAs) were investigated by systematically varying transition metals instead of Al, within the chemical formula of Al_2M_{14} (M represents different mutations of transition metals). The formation of different crystal structures (FCC, BCC, or FCC+BCC mixture) and its effects on the resulting mechanical properties of this series of HEAs, both in tension and compression, were evaluated. It was found that, in the BCC-dominated HEAs, ordered B2 precipitates were always coherently dispersed in the BCC solid-solution matrix. The shape of these B2 precipitates was strongly affected by the lattice misfit between the disordered BCC and ordered B2. A uniform distribution of cuboidal B2 particles could be obtained by properly adjusting M, thus the lattice misfit, in a manner similar to that in Ni-based superalloys. Strengthening effects caused by different BCC/B2 morphologies were also estimated and compared with experimental measurements. The optimal strengthening as a function of the shape and size of the coherent precipitates was discussed in light of the lattice misfit in these HEAs.

1. Introduction

The development of new types of metallic materials always draws large attention from materials community because of the potential of engineering applications. Traditional design of structural alloys is to select the principal element based on a specific property requirement, and further to use alloying additions to confer secondary properties without sacrificing the primary property. Such design concept has led to the development of many advanced alloys and, over the past few decades, significant knowledge and theories about alloys based on one principal component have been accumulated. Recently, a new class of compositionally complex alloys, namely, high-entropy alloys (HEAs) or multi-principal elements alloys (MPEAs), has developed and these alloys exhibited many unique properties, for example, high strength/ductility and good fracture toughness [1–6]. Different from the traditional alloys, HEAs generally contain multiple principal elements (>5) in equimolar or near-equimolar proportions and often have a simple crystal structure, e.g., face-centered cubic (FCC), body-centered cubic (BCC), hexagonal close-packed (HCP) solid solutions, or their ordered derivatives (such as *cP*4-$AuCu_3$ ($L1_2$) and *cP*2-CsCl (B2)) [5–8]. Interestingly, common strengthening mechanisms found in traditional alloys, such as solid solution strengthening [9], precipitation strengthening [10,11], dislocation and grain boundary strengthening [12], as well as TWIP (twinning-induced plasticity) and TRIP (transformation-induced plasticity) effects [13,14], have all been reported to occur in HEAs.

Based on the constituent elements, HEAs can be classified into three types: late transition metals (LTMs, e.g., Mn, Fe, Co, Ni, Cu)-based FCC HEAs [12–21], early transition metals (ETMs, e.g., Ti, V, Mo, W)-based BCC refractory high-entropy alloys (RHEAs) [22–26], and Al-TMs HEAs (including mixed ETMs and LTMs) with dual-phase structures (FCC+BCC) [27–36]. A large variety of crystal phases and microstructures render HEAs with diverse properties, especially mechanical properties. For example, an FCC single-phase CoCrFeMnNi HEA (also known as Cantor Alloy), as a result of easy twinning in the material, exhibited a higher work hardening

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capability and improved ductility than all the traditional alloys at cryogenic temperatures [15]. Some metastable HEAs with a non-equimolar mixing of elements also showed prominent mechanical properties induced by either TWIP or TRIP effect [13,14]. The highest strength has been reported in BCC-based RHEAs, such as CrNbTiVZr [22]. In the case of Al-LTM HEAs, in particular, the mechanical properties appeared to be tunable because of their microstructural diversities. An $Al_{0.5}NiCoFeCrCu$ HEA [30], which has a dual-phase FCC/BCC structure, exhibited a higher tensile strength than the single-phase FCC ($Al_xNiCoFeCr$) HEAs with the Al content less than 0.3 [32–35].

For material strengthening, it has been demonstrated that, through alloying, coherent spherical $L1_2$-$Ni_3(Al, Ti)$ particles were produced in an FCC $(FeCoNiCr)_{94}Ti_2Al_4$ HEA (in atomic percent, at. %) which led to a significant strength improvement [10]. This result is intriguing since precipitation hardening is well known to occur in traditional Ni-based and Co-based superalloys with γ-FCC/γ′-$L1_2$ microstructures [37–39], in which the mechanism actually dominates the high-temperature performance. However, despite of the fact that precipitation strengthening has been widely reported in FCC-based alloys, the mechanism appears to occur much less often in BCC-based alloys. Coherent nanoprecipitation has not yet been developed to enhance ultra-high strength ferritic steels [40,41]. It was fascinating to note that, in a recent study of a BCC lightweight $AlMo_{0.5}NbTa_{0.5}TiZr$ HEA, cuboidal BCC particles were observed to coherently embed in the B2 matrix, besides some plate-like BCC precipitates [27]. In addition, alloying Al to FCC-HEAs has been recognized and frequently used to shift the structure from FCC to BCC for the strength improvement [31–35]. However, in the high Al-containing BCC HEAs, the B2 and BCC phases often form a weave-like microstructure, as a result of spinodal decomposition [31–35]. Consequently, the plasticity of these BCC HEAs is severely deteriorated, for example, the high-strength AlNiCoFeCr has virtually no tensile ductility [31]. It is challenging, but highly desirable, to produce microstructures with a uniform distribution of ordered B2 particles in disordered BCC alloy matrix.

Whereas adjusting the Al content is frequently used to alter the microstructures of Al-TM HEAs [32–35], there was limited or no effort to study the role of transition metals. Therefore, in this study, we aim at investigating the microstructural evolution and the corresponding mechanical properties of the Al-Ni-Co-Fe-Cr (Al-TM) alloy system by mutating the transition metals, instead of varying the Al content. The HEAs used for this study are designed based on the cluster formula approach we recently developed [42,43]. The shape and size of the coherently-precipitated BCC or B2 particles formed in these HEAs will be discussed in light of lattice misfit. Strength improvement caused by the presence of coherent B2 precipitates in BCC-dominant alloys will be analyzed and the stability of these precipitates at high temperatures will also be addressed.

2. Composition design of Al-Ni-Co-Fe-Cr HEAs based on the cluster formula approach

The cluster formula approach [42,43] used for the design of alloy compositions was based on the chemical short-range orders (CSROs) in solid solutions proposed initially by Cowley [44] and Friedel [45]. The stronger CSROs (denoted as the nearest-neighbor clusters centered by a solute atom having strong interaction with the base solvent atoms) are interconnected by additional atoms (i.e. glue atoms with weak interactions) to form dense-packed 3D structure. In essence, this cluster approach visualizes CSROs in a solid solution as a local structural unit consisting of a nearest-neighbor cluster surrounded by several glue atoms. Consequently, a composition formula of $[cluster](glues)_m$ can be obtained, in which the nearest-neighbor clusters are cuboctahedron with a coordination number of 12 (CN12) and a rhombi-dodecahedron with CN14 in FCC and BCC solid solutions, respectively [42,43]. Since HEAs can be treated as a special kind of solid solution alloys, CSROs have been confirmed in some HEAs by both neutron scattering experiments and simulations [46–48]. Thus, it is conceivable that the cluster formula approach can also conveniently extend to HEAs; in fact, the cluster model was recently validated in HEAs by neutron experiments [49].

In Al-TM HEA systems, Al interacts strongly with transition metals, while TMs are expected to exhibit only weak mutual interactions, as indicated by the enthalpies of mixing ΔH [50]. For Al-Ni-Co-Fe-Cr, the enthalpies of mixing between Al-TM are $\Delta H_{\text{Al-Ni}} = -22$ kJ mol^{-1}, $\Delta H_{\text{Al-Co}} = -19$ kJ mol^{-1}, $\Delta H_{\text{Al-Fe}} = -11$ kJ mol^{-1}, and $\Delta H_{\text{Al-Cr}} = -10$ kJ mol^{-1}, much higher than those between TMs (enthalpies of mixing are nearly to zero [50]). Consequently, when applying the cluster formula approach to this system, all the TMs can be simply treated as a single virtual element M of the base solvent and Al serves as the solute element. Thus, the $Al_xNiCoFeCr$ HEA series can be simply expressed by the pseudo-binary Al_xM_4, where $M = Ni_1Co_1Fe_1Cr_1$ is the equimolar mixing of TMs. Following this notion, the alloy composition of Al_2M_{14} ($Al_{12.5}M_{87.5}$, at. %), derived from the cluster formula for either the FCC ($[Al\text{-}M_{12}](M_2Al_1)$) or BCC ($[Al\text{-}M_{14}]Al_1$) structures, is actually close to the upper limit of the Al-content (i.e., $Al_{11.1}M_{88.9}$ or $Al_{0.5}M_4$) reported in the single-phase FCC-$Al_xNiCoFeCr$ alloys [32]. The crystal structures of Al_2M_{14} HEAs might be varied through changing the proportion of M from an equimolar mixing of TMs to a non-equimolar mixing, since all these TMs are different FCC- or BCC-stabilized elements.

Therefore, in the present work a series of new Al-Ni-Co-Fe-Cr HEAs are designed and synthesized based on the composition formula Al_2M_{14}, in which Al is fixed and M represents different mutations of the four transition metals. These alloys are specifically denoted as $M_{1111} = Ni_1Co_1Fe_1Cr_1$ (No.1 alloy in Table 1), $M_{4433} = Ni_4Co_4Fe_3Cr_3$ (No.2), $M_{1121} = Ni_1Co_1Fe_2Cr_1$ (No.3), and $M_{1112} = Ni_1Co_1Fe_1Cr_2$ (No.4). To evaluate the effect of Al addition, another alloy with a higher Al content, specifically, Al_3M_{14} ($M = Ni_1Co_1Fe_1Cr_1$) (No.5) was also synthesized and studied. These alloys and their specific chemical compositions (at. %) are summarized in Table 1.

3. Experimental

Alloys used in this study were prepared by means of arc melting and suction cast into a 6 mm-diameter cylindrical copper mold under an argon atmosphere. Purities of the raw elemental metals are 99.99% for Al, Co, Fe, and Ni, and 99.9% for Cr, respectively. Mixtures of raw materials with appropriate compositions and a total weight of about 15 g were remelted at least four times to ensure chemical homogeneity before suction-casting. In order to investigate the microstructural stability of coherent precipitates at high temperatures, No.4 alloy samples ($M_{1112} = Ni_1Co_1Fe_1Cr_2$) with a size of $\phi 6 \times 8$ mm were additionally heat-treated at temperatures of 673, 873, 973, and 1073 K for 2 h and, then, followed by water-quenching.

Crystalline phases in these as-cast alloys were identified using a Bruker D8 X-ray diffractometer (XRD) with the Cu-K_α radiation ($\lambda = 0.15406$ nm), in which the external standard method was applied to calculate the lattice constants [51]. The microstructure was examined using either Olympus optical microscopy (OM), Zeiss Supra 55 scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS), Philips Tecnai G^2 transmission electron microscopy (TEM) equipped with a selected-area electron diffraction (SAED) analysis, or Tecnai F30 scanning transmission electron microscopy (STEM). The etching solution used for sample