A novel method to enhance CSL fraction, tensile properties and work hardening in complex concentrated alloys — Lattice distortion effect

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A B S T R A C T

A framework has been developed to reduce the stacking fault energy of complex concentrated alloys (CCAs) or high entropy alloys based on increasing lattice distortion by choosing principal elements with large differences in moduli and atomic size. The framework and selection criteria have resulted in the inclusion of five CCA compositions for validation of the lattice distortion and three Fe-containing CCAs. Orientation imaging microscopy (OIM) was used to examine the fraction of special boundaries in all of the CCAs. Alloys with large lattice distortion contained high density of annealing twins. Both tensile properties and work hardening rate characteristics were evaluated. CCAs that were designed based on lattice distortion demonstrated improved ultimate tensile strength. Work hardening rate curves revealed the underlying variation in the tensile properties of various CCAs. For selected alloys, post-deformation OIM analysis of the lateral surface was carried out for establishing defect density variation.

1. Introduction

A new class of alloy systems with multi-principle elements in equi- or non-equi-atomic compositions has been developed [1,2]. Recently, these alloys have been more broadly termed as complex concentrated alloys (CCAs), which include high entropy alloys (HEAs). Alloys with a minimum of five elements in equimolar or non-equimolar quantities have generally been referred to as HEAs, while alloys with intermetallic phases and three principal elements are broadly referenced as CCAs [3]. The unique feature of these alloy systems is that no dominant element can be designated as the matrix element. This lack of a dominant element is a breakthrough in materials science, with the shift in compositional space from the edges or apexes of a phase diagram where one element is dominant, to the center where multiple elements are dominant. In certain compositions, mixtures of multiple principal elements have crystallized in simple face-centered cubic (FCC) [4], body-centered cubic (BCC) [4], or hexagonal close-packed (HCP) [5] crystal structures. The core effects in CCAs are the sluggish diffusion of atoms, lattice distortion, high entropy effect, and cocktail effect [6]. The presence of multiple elements of various sizes, moduli, and cohesive energy differences have been known to increase lattice distortion by shifting the elements from their FCC or BCC reference positions [7–9].

Mishra et al. [10] proposed a lattice distortion framework for designing alloys to specifically increase lattice distortion in CCAs so that fundamental deformation mechanisms could be tuned. Distortion of the lattice would have implications on the stacking fault energy (SFE), lattice friction stress, and energetics and kinetics of dislocations and twins.

SFE has been identified as a crucial parameter in the plastic deformation of conventional FCC metals and alloys, as it determines the separation distance between the two partials and, more importantly, the twinning probability. The lowest SFE values have been noted for the conventional solid solution alloy Cu-8 wt% Al as $2.5 \, \text{mJ/m}^2$ [11] and for the non-equiatomic CCA $Fe_{20}Cr_{26}Ni_{14}Co_{20}Mn_{20}$ as $3.5 \, \text{mJ/m}^2$ [12]. CrCoNi [13,14], a ternary medium entropy alloy, exhibited better tensile strength, ductility, and cryogenic fracture toughness than quinary CrMnFeCoNi CCA [15]. This was attributed to twinning induced plasticity (TWIP), which was higher in ternary CCA when compared to quinary CrMnFeCoNi CCA. In CrCoNi and CrMnFeCoNi CCAs, deformation nano-twins led to excellent cryogenic properties, second only to cryogenic steels [15]. Furthermore, in-situ transmission electron microscopy analysis revealed that nano-twins formed in front of the propagating crack, effectively bridging the propagating crack [16]. The extent of twinning or twinnability is directly correlated to SFE and both ductility and strength typically increase with the reduction in SFE. As

discussed previously, alloying additions have always been key to modifying the SFE of various alloy systems. In CCAs, given the nature of the lattice, modifying the lattice distortion could also produce a reduction in SFE.

Lattice distortion in CCAs has been observed in experimental and modeling investigations [7–9,17]. As compared to FeCoCrNi and Fe-CoCrNiMn CCAs, Pd added FeCoCrNi CCA exhibited the largest mean lattice distortion, specifically due to large atomic size mismatch between Pd and the remaining atoms in the matrix. In these alloys, Cr-Cr and Mn-Mn atom pairs also had the largest bond distance among the remaining combinations [7]. Furthermore, pair distribution function based analysis revealed that lattice distortion of FeCoCrNiPd CCA was two times as compared to Ni80Pd20 alloy [8]. In another investigation, mean-square atomic displacements obtained from synchrotron X-ray diffraction measurements for various ternary, quaternary, and quinary CCAs correlated well with the shear modulus normalized yield strength [17]. In an investigation on Co16.67Fe36.67Ni16.67Ti30 CCA using molecular dynamics simulation, Ti atoms created large static distortions and misfit strain center, leading to large lattice distortion [9].

Overall, these investigations pinpoint two methods to increase lattice distortion in CCAs, (a) introducing relatively large atoms in the matrix of similar-sized atoms, and (b) introducing more Cr atoms that would increase lattice distortion via large bond length. In the current investigation, both of these concepts were employed to create alloy compositions that would exhibit large lattice distortion. CrCoNi was taken as the reference alloy and alloying additions were made to modify the lattice distortion. First, the conceptual framework supporting the current investigation has been presented, and this is followed by alloy selection criteria. In total, eight CCAs were produced, and both one-step recrystallization analysis and mechanical characterization via tensile testing were carried out. A detailed work hardening mechanism study was followed by post-deformation analysis.

2. Experimental methods

$Al_{0.1}CrFeCoNi$ alloy was procured in the cast form from Sophisticated Alloys, Inc. Other seven alloys were produced from pure elements via vacuum arc melting using Al (99.9% purity), Co (99.3% purity), Fe (99.98% purity), Ni (99.95 +% purity), Ti (99.99% purity) and Cr (99.3% purity) elements. During the melting process, alloys were flipped six times to ensure chemical homogeneity in a cigar-type cast. Homogenization was conducted at 1473 K for 6 h in Ar atmosphere to further remove remnant chemical heterogeneities. After removing the thin oxide layer in the homogenized pieces, all alloys were subjected to cold-rolling reduction of ~85%. Next, one-step recrystallization was carried out at 1000 °C for 30 min in air followed by water quenching. By using a high annealing temperature, no secondary phases were formed in the microstructure. After recrystallization, samples were cut for electron back scattered diffraction (EBSD) analysis. Coarse polishing was performed using SiC papers, while 1 μm and 0.05 μm surface finish polishing were performed using colloidal diamond and silica suspensions, respectively. An FEI Nova NanoSEM 230 with Hikari Super EBSD system enabled orientation imaging microscopy (OIM). TSL OIM™ software was used to analyze various orientation-related information. The same EBSD acquisition area of $250 \times 250 \, \mu m^2$ at a step size of 0.8 μm was chosen for all alloys, and two scans were run per condition to confirm reliability. Tensile testing was carried out for all compositions at initial strain rate of $10^{-3} \, s^{-1}$. Rectangular dog bone specimens with dimensions of ~5 mm gage length, ~1.23 mm width, and 1.0–1.1 mm thickness were fabricated using a CNC milling machine. All tensile samples were polished down to ~1 μm surface finish. Tensile testing was performed using a custom-built, computer-controlled tensile testing frame equipped with a 500-pound load cell. Post-deformation analysis, specifically kernel average misorientation (KAM) analysis were carried out for $Al_{0.1}CrFeCoNi$ and $Al_{0.1}CrCoNi$ compositions. Surfaces were again polished using the same

methodology described above for EBSD sample preparation. For OIM data acquisition, a fine step size of 0.3 μm was used for both scans. Fractography analysis was also carried out using a FEI Quanta 200 environmental scanning electron microscope.

3. Results and discussion

3.1. Conceptual framework

SFE is a thermodynamic quantity that denotes the ability of elements with FCC atomic stacking to exhibit an HCP stacking sequence. In pure metals, SFE is determined by bond directionality (electronic structure), and low SFE is observed in materials with less bonding directionality, for instance Cu. In alloys, solutes modify the electronic structure of the matrix element such that SFE can either be increased or decreased with alloying additions. Furthermore, solutes also tend to segregate in stacking faults, thereby stabilizing the faulted sequence, a behavior generally known as Suzuki segregation. In the case of CCAs, there is a possibility for all of these effects to occur. In addition, lattice distortion can also be significant in modifying SFE. Distorting the lattice locally always occurs in solid solution strengthening, in which a larger or smaller element (compared to the matrix) distorts the local atomic arrangements, lowering the dislocation core energy, and eventually pinning the dislocations. In the case of CCAs, the presence of multiple elements in equi-atomic fractions distorts the lattice globally rather than just locally.

The complex interactions between multiple constituents and the consequent distortion leads to a shift in the position of atoms from their ideal FCC packing positions. In simplistic terms, the CCA lattice is distorted as compared to the ideal FCC lattice of a pure element, and the CCA exhibits a non-ideal FCC stacking. It has been well-known for decades that low SFEs result in easier formation of stacking faults and twins. In a distorted lattice, the ground state energy of an FCC crystal will be higher than the undistorted FCC lattice due to the contribution from the strain energy of distorted bonds. In this scenario, when a fault in the FCC stacking sequence is created by shuffling the atoms, the faulted HCP region will also possess non-ideal HCP stacking. Recent DFT investigations in CoCrNi CCA have observed an interesting phenomenon at 0 K in which the HCP stacking sequence exhibited low free energy when compared to FCC stacking, making HCP stacking more stable [18]. At 300 K, the contribution from lattice vibrations made FCC stacking more stable as compared to HCP stacking. Given these unique observations, the energy state of non-ideal HCP stacking of the faulted region in FCC stacking could be lower than ideal HCP stacking. Overall, the energy difference between HCP and FCC stacking ($\Delta E^{HCP-FCC}$) in the distorted condition was lower than the undistorted condition and could be given as:

$$(\Delta E^{HCP-FCC})_{Distorted} \ll (\Delta E^{HCP-FCC})_{Undistorted} \qquad (1)$$

Therefore, increasing the lattice distortion would increase the energy state of FCC, thereby making a large fraction stacking faults and twins energetically favorable. This framework for reducing the SFE by increasing the lattice distortion of CCAs is shown in Fig. 1. The conventional discussion on the effect of alloying additions on SFE is also presented (right side). The correlation between lattice distortion and the natural tendency to form faults is important in designing CCAs that possess excellent twinnability and work hardenability.

3.2. Selection criteria to increase lattice distortion

As mentioned previously, multiple formulations such as ΔS_{mix}, δ, $\Delta \chi$, and VEC have been used to differentiate the compositions that led to solid solutions and the formation of intermetallic second phases [19]. In addition to thermodynamic formulations, there are formulations that correlate lattice distortion to computable quantities. These formulations are based on inter-atomic distance mismatches whose results are similar