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Phase equilibria in equiatomic CoCuFeMnNi high entropy alloy

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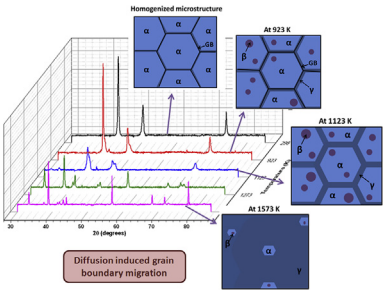
HIGHLIGHTS

- The phase stability of the newly developed CoCuFeMnNi HEA was investigated.
- Detailed analysis showed that the metastable FCC HEA α phase decomposes into β and γ at higher temperatures.
- The CALPHAD predictions are successful in predicting the formation of BCC and second FCC phase.
- Moreover, embrittlement of alloy will not occur throughout the temperature regime because the phases are not brittle in nature.

GRAPHICAL ABSTRACT



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ABSTRACT

Phase equilibria and stability of a newly developed single phase equiatomic CoCuFeMnNi high entropy alloy (HEA) was investigated in the temperature range of 298–1573 K using in situ high temperature X-ray diffraction and thermodynamic modeling using CALPHAD (CALculation of PHAse Diagrams) approach. Complimentary characterization techniques like scanning and transmission electron microscopy with energy dispersive spectroscopy for microstructural investigation and compositional analysis, differential scanning calorimetry for thermal analysis and atom probe tomography for near-atomic scale chemical analysis were employed. It was found that the metastable FCC solid solution α phase (lattice parameter = 0.361 nm) undergoes phase transformation at 923 K and 1123 K. The α phase transforms to BCC β phase (a = 0.280 nm) at 923 K and on further heating, another FCC phase γ (a = 0.362 nm) precipitates out at 1123 K, leading to coexistence of two FCC phases and one BCC phase. Atom Probe Tomography carried out to study the three-dimensional distribution of constituent elements indicates the presence of ~2 nm sized Cu clusters in the α phase. CALPHAD predictions indicate the tendency towards phase separation involving iron-cobalt and copper to partition out of the equiatomic solid solution to form the BCC and second FCC phase, respectively. A qualitative agreement between CALPHAD predictions and in situ high temperature X-ray diffraction accompanied with complimentary characterization tools explicitly demonstrates the fidelity of CALPHAD modeling for the design and development of novel HEA compositions.

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1. Introduction

Over the last decade the field of alloy design has ventured into unknown compositional space with the advent of multiprincipal multicomponent high entropy alloys (HEAs) comprising of five or more elements in equal or near-equal proportions. These alloys are characterized by their unusually high configurational entropy of mixing ($\Delta S_{config} \geq 1.5R$) and have attracted worldwide interest due to their unique characteristics as well as attractive properties [1–6]. HEAs derive their name from the high configurational entropy of mixing associated with them, however, additional contributions from vibrational, electronic and magnetic entropy in determining phase stability has been highlighted recently [7]. There are very large combinations of possible HEAs, and studying each and every one of them requires sustained effort and time. Hence, a robust technique for screening of novel HEA combinations is warranted. A new strategy involving rapidly evaluating structural HEAs has been proposed by Miracle et al. [8]. It consists of three stages of evaluation. Stage 0 is known as phase diagram evaluation (via CALPHAD calculations), whereas stage 1 is related to evaluating properties based on composition but insensitive to microstructure and stage 2 involves evaluating properties which are strongly dependent on microstructure. This strategy primarily relies on the rejection of candidates, narrowing down the number of candidates for subsequent investigation. Till date only two equiatomic single phase quinary alloys namely CoCrFeMnNi developed by Cantor et al., in 2004 [9–11]; and CoCuFeMnNi developed by the present authors has been investigated [12,13].

It is to be noted that single phase HEAs are model material for studying complex concentrated alloys, as they have the highest configurational entropy of mixing. This makes them important from technological as well as scientific point of view. Various techniques, such as experimental phase diagram inspection, CALPHAD (computational thermodynamic approach), AIMD (*ab-initio* molecular dynamics) simulations, DFT (density function theory) calculations as well as Monte Carlo simulations have been employed to unearth new single phase HEAs but with limited success [14]. Parametric approach, based on empirical rules is computationally less demanding than other methods but has low success rate [15]. CALPHAD is considered to be the only technique that is based on a thermodynamic background and is less computationally demanding [16]. It offers phase evolution in an alloy system as a function of temperature and minimizes the experimental efforts for determining the phase diagram of multicomponent alloys.

Otto et al. [17]. have studied the thermal stability of the Cantor alloy (CoCrFeMnNi) and have reported that the HEA phase is not stable at lower temperatures (<975 K). In fact, HEA phase in equiatomic CoCrFeMnNi alloy is found to undergo phase transformation to produce $L1_0$ FeMn and BCC phases (Fe-Co and σ). Some of these phases, especially σ phase are brittle in nature and can cause embrittlement of the alloy during prolonged exposure at intermediate (773–1173 K) temperature. Thus, it is important to study thermal stability of the alloy under investigation. The stability of HEAs is of paramount importance because these novel materials are now considered for potential applications. The studies on thermal stability of HEA phases at different temperatures are sought after in the community [18]. In the present investigation, phase evolution of CoCuFeMnNi HEA has been studied using in situ high temperature X-ray diffraction, scanning and transmission electron microscopy and atom probe tomography. The experimental results have been verified with predictions from CALPHAD to determine the ability and efficiency of thermodynamic modeling for predicting phase evolution in HEA.

2. Material and methods

High purity elemental pieces (>99.9%) were used to synthesize as-cast buttons (approx 10 g each) of equiatomic CoCuFeMnNi HEA, using vacuum arc melting under argon atmosphere, in a water cooled copper hearth, with non-consumable tungsten electrode. The alloy buttons were flipped and remelted at least five times to ensure chemical homogeneity. This was followed by suction casting the alloy in the vacuum arc melting cum suction casting facility. A rod of square cross-section with dimensions 10 mm × 10 mm × 60 mm was obtained, which was subsequently sealed in a quartz tube under argon gas atmosphere and homogenized at 1273 K for 7 days, followed by quenching in water.

3. Experimental

3.1. Thermodynamic calculations using CALPHAD

CALPHAD approach is based on global minimization of Gibbs free energy as a function of temperature and composition. Computational software as well as thermodynamic databases are very necessary for application of this method. The thermodynamic database consists of thermochemistry and phase equilibrium data, which is obtained from first principle calculations. The thermodynamic description of a system is included in the database containing Gibbs free energy functions of the phases, constructed using a suitable solution model [19]. Binaries and ternaries are extrapolated to higher order systems and the details of the present approach can be obtained in an earlier publication [11]. In order to understand the phase formation, detailed calculations were performed using HEA database (TCHEA1 v1.0) in CALPHAD and property diagram as well as pseudo binary phase diagram of the HEA was constructed.

3.2. Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) was carried out using TGA/DSC 1 (Mettler Toledo, Switzerland), in the temperature range of 303 K–1373 K, with heating rate of 10 K/min heating rate. Argon gas was used to maintain inert atmosphere, 20 mg of alloy was used in an alumina crucible.

3.3. In situ high temperature X-ray diffraction

Thin sections (10 mm × 10 mm × 1 mm) from the homogenized sample were machined and polished using emery papers for in situ high temperature X-ray diffraction using PANalytical X-pert diffractometer (Panalytical, USA) with an Anton Parr furnace. The samples were placed on a platinum holder, and inert atmosphere was maintained inside the furnace using argon gas. The samples were heated from 298 K to 1573 K at 10 K/min heating rate. XRD scans were measured at 298, 723, 773, 823, 873, 923, 973, 1023, 1073, 1123, 1173, 1223, 1273, 1373, 1473 and 1573 K after a holding time of 45 min at each temperature. Ni-filtered CuKα radiation ($\lambda = 0.154$ nm) was used, with 45 kV voltage and 40 mA current. Step size of 0.2° was used for a scan range of 30–85°.

3.4. Scanning and transmission electron microscopy

The samples for SEM were metallographically prepared by polishing with emery papers, followed by 1 μm alumina cloth polishing until mirror finish was achieved. The microstructure was observed under Nova NanoSEM 450 Field Emission Scanning Electron Microscope (FEI, Netherlands) using 4 quadrant BSE detector and compositional analysis was carried out using Energy