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# Structural evolution during mechanical milling and subsequent annealing of Cu–Ni–Al–Co–Cr–Fe–Ti alloys

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ABSTRACT

This study reports the structural evolution of high-entropy alloys from elemental materials to amorphous phases during mechanical alloying, and further, to equilibrium phases during subsequent thermal annealing. Four alloys from quaternary $Cu_{0.5}NiAlCo$ to septenary $Cu_{0.5}NiAlCoCrFeTi$ were analyzed. Microstructure examinations reveal that during mechanical alloying, Cu and Ni first formed a solid solution, and then other elements gradually dissolved into the solid solution which was finally transformed into amorphous structures after prolonged milling. During thermal annealing, recovery of the amorphous powders begins at 100 °C, crystallization occurs at 250–280 °C, and precipitation and grain growth of equilibrium phases occur at higher temperatures. The glass transition temperature usually observed in bulk amorphous alloys was not observed in the present amorphous phases. These structural evolution reveal three physical significances for high-entropy alloys: (1) the annealed state of amorphous powders produces simple equilibrium solid solution phases instead of complex phases, confirming the high-entropy effect; (2) amorphization caused by mechanical milling still meets the minimum criterion for amorphization based on topological instability proposed by Egami; and (3) the nonexistence of a glass transition temperature suggests that Inoue's rules for bulk amorphous alloys are still crucial for the existence of glass transition for a high-entropy amorphous alloy.

## 1. Introduction

Multiple elements can be added to conventional alloys, such as Fe- (steel), Cu-, Al-, Ti-, Mg-, and Ni-based alloys, to improve their properties including strength, toughness, and wear, oxidation, and corrosion resistances. However, the amount of these additives is generally limited to low levels to prevent the formation of a lot of intermetallic compounds, effectively limiting alloys to one principal element. In 1995, Yeh et al. started to explore new alloys with multi-principal elements. These alloys are called "high-entropy alloys" (HEAs) [1–7], and are composed of at least five principal elements in equal or near equal mole ratios. Compared with traditional alloys, the relatively high mixing entropies of HEAs largely reduce the free energy of simple solid solution phases and make them more stable than intermetallic compounds, especially at high temperatures [3,5]. Previous studies report many phenomena and properties of HEAs, including (1) the tendency to form simple face-centered cubic (FCC) and/or body-centered cubic (BCC) solid solutions, (2) the tendency to have nano-sized precipitations and even amorphous phases, and (3) the tendency to exhibit high thermal stability, high hardness, and excellent corrosion resistance [8–14].

Since HEAs are a brand-new field of alloy research, further efforts are needed to elucidate their fundamental characteristics, and especially their thermodynamic and kinetic aspects, which govern the phase equilibrium and transformation. Previous studies usually make microstructure characterizations and property investigations of cast HEA bulks [1–14]. However, this cast-route approach is difficult to reveal some important thermodynamic and kinetic behaviors such as the equilibrium structure because of the segregation problem during solidification. Although homogenization treatments can be used to obtain the equilibrium structure without segregation and non-equilibrium phases, it would require a long treatment time due to the relatively slow diffusion of HEAs.

Mechanical alloying (MA) is a common powder manufacturing process which can fabricate homogeneous materials from elemental powders [15]. MA powders are generally in a non-equilibrium state since high-energy milling process places severe strains to them. Therefore, the thermodynamic-equilibrium phases of amorphous MA powders can more easily be obtained by short thermal annealing. Although some studies on the thermal stability of amorphous multi-component alloy powders prepared by MA [16–18] have examined up to seven components [16], most of these studies

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**Table 1**
Nominal composition of experimental alloys (at.%).

| | Cu | Ni | Al | Co | Cr | Fe | Ti |
|---|---|---|---|---|---|---|---|
| $Cu_{0.5}NiAlCo$ | 14.2 | 28.6 | 28.6 | 28.6 | | | |
| $Cu_{0.5}NiAlCoCr$ | 11.1 | 22.2 | 22.2 | 22.2 | 22.2 | | |
| $Cu_{0.5}NiAlCoCrFe$ | 9.1 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | |
| $Cu_{0.5}NiAlCoCrFeTi$ | 7.7 | 15.4 | 15.4 | 15.4 | 15.4 | 15.4 | 15.4 |

are based on one principal element with a concentration more than 50 at.%. Thus, it is important to extend our understanding to HEAs by investigating the thermodynamic and kinetic phenomena in alloy systems with multi-principal elements in equal or near equal mole ratios.

This study reports the preparation of a series of HEA powders of Cu–Ni–Al–Co–Cr–Fe–Ti prepared by MA and then thermally annealed. This approach reveals the thermodynamic and kinetic aspects of HEA powders through structural evolution from elemental materials to amorphous phases and then to equilibrium phases. For comparison, HEA cast bulks with same compositions as the MA alloys were also prepared by arc melting. The differences between the constituent phases of the cast bulks and annealed powders can be useful to reveal the deviation of the cast structure from equilibrium structure.

## 2. Experimental

Four MA specimens, including quaternary $Cu_{0.5}NiAlCo$, quinary $Cu_{0.5}NiAlCoCr$, senary $Cu_{0.5}NiAlCoCrFe$, and septenary $Cu_{0.5}NiAlCoCrFeTi$ alloys (all expressed in molar ratio), were prepared. Table 1 lists the nominal compositions of experimental alloys. Elemental powders of Cu, Ni, Al, Co, Cr, Fe, and Ti with purities higher than 99.9% were used as raw materials. Their average particle sizes were 5, 10, 25, 5, 5, 40, and 30 μm, respectively. In the first step of the MA process, the various elemental powders were charged into hardened SKD 11 (JIS G4404 SKD-11) steel vials with a hardness of RC 50 together with chrome steel balls (6.4 mm in diameter and 10:1 in ball-to-powder weight ratio) and sealed under an argon atmosphere. Milling was then performed in an SPEX 8000 vibration ball-milling machine for 1, 2, 3, 4, 6, 12, 24, 36, 48, and 60 h, respectively. To avoid a significant increase in temperature, the steel vials were cooled by a continuous air flow, and an interval of 10 min was applied after each milling cycle of 30 min. The amorphous MA powders obtained after a prolonged milling time were further sealed in quartz tubes, evacuated to 0.01 atm, and then annealed at designated high temperatures for 30 min.

For comparison, cast bulks with the same compositions as the MA alloys were prepared by arc melting raw elements of at least 99% purity. The melt was then solidified in a Cu crucible under a vacuum of 0.01 atm [3]. The bulk samples were cut, ground, polished, and etched by aqua regia for microstructure observations.

Thermal analysis was performed with a differential thermal analyzer (DTA, Pyris Diamond) from room temperature to 1300 °C at a heating rate of 10 °C $min^{-1}$ in an argon atmosphere. An X-ray diffractometer (XRD, Rigaku ME510-FM2) with Cu $K_\alpha$ radiation (1.5405 Å) was carried out to analyze the crystal structures of the MA powders and cast bulks at a scanning speed of 4° $min^{-1}$. A scanning electron microscope (SEM, JEOL-5410) with an energy dispersive spectrometer (EDS) was used to observe microstructures and measure the composition of alloy powders. The amorphous powders were also investigated by transmission electron microscope (TEM, JEOL-2010) for confirmation.

## 3. Results

### 3.1. Phase evolution of elemental powders during MA

Fig. 1 shows the XRD patterns of the quaternary $Cu_{0.5}NiAlCo$ MA powders with different milling times. In the early stages of milling, the diffraction peaks of Cu and Ni first merge and broaden, implying the formation of a FCC Cu–Ni solution, as explained in previous research [19,20]. At the same time, the peaks of Al and Co decrease in intensity and disappear in sequence, implying the dissolution of Al and Co into the Cu–Ni solution phase. This dissolution is caused by severe deformation enhanced diffusion even at low milling temperatures. With prolonged milling, the Cu–Ni solution diffraction peaks shift to a lower angle, indicating lattice expansion due to the dissolution of the larger element, Al [19,20]. After milling for 6 h, only one set of peaks of the FCC solid solution appears, with no peaks of residual pure elements. The grain size ($d$) of the FCC solution phase calculated by the Scherrer equation [21] ranges from 4.4 to 5.5 nm at milling times ranging from 6 to 48 h. After milling for 60 h, the MA powders become amorphous, indicating the complete deconstruction of crystalline structures by severe mechanical deformation. Similar phase evolution occurs in the other three MA powders as well. Fig. 2 plots the XRD patterns of each alloy, which show the amorphous structures obtained after extended milling. However, there are still some small protrusions in the patterns besides the broad amorphous peak, indicating that a small amount of nanocrystalline phase exists in the powder samples. The crystalline phase is considered to be from those particles with a partial amorphous structure. TEM analysis confirms the presence of these amorphous structures. Fig. 3 shows a typical TEM image of $Cu_{0.5}NiAlCoCr$ amorphous powders. The bright field image in Fig. 3(a) exhibits no structural contrast but only thickness contrast, which corresponds to the diffraction pattern showing only amorphous diffuse ring. By choosing a part of the diffuse ring, the dark field image shows a bright matrix dispersed with many bright spots which are smaller than 1 nm, as Fig. 3(b) shows. Although some spots larger than 1 nm still exist, as marked by the circles, the

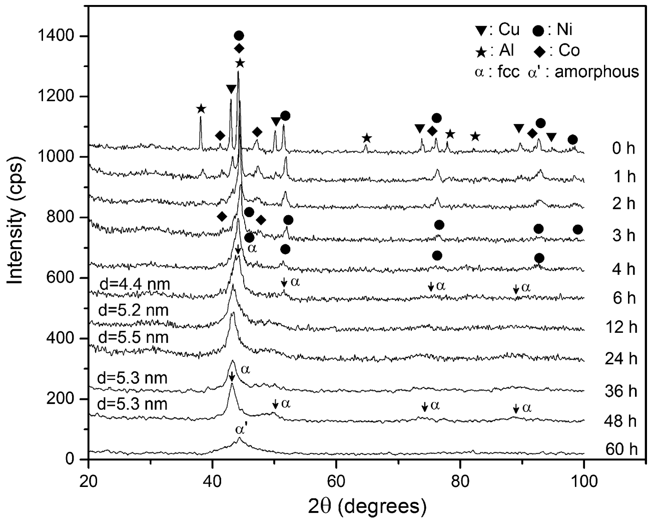

**Fig. 1.** XRD patterns of MA quaternary $Cu_{0.5}NiAlCo$ powders with different milling times.

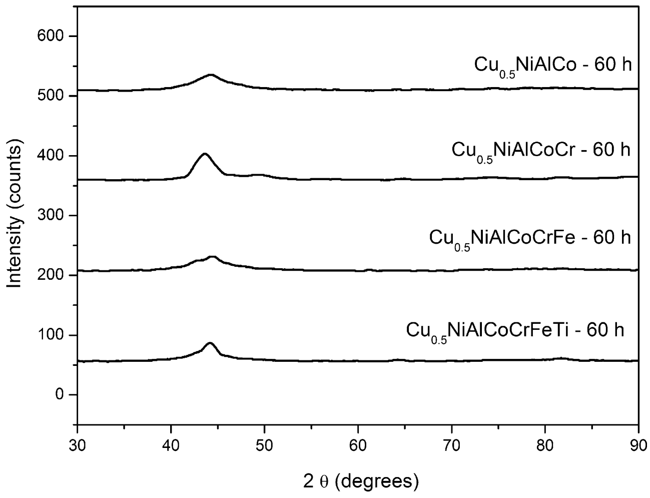

**Fig. 2.** XRD patterns of amorphous MA quaternary $Cu_{0.5}NiAlCo$ to septenary $Cu_{0.5}NiAlCoCrFeTi$ powders after milling for 60 h.