



In-situ high throughput synthesis of high-entropy alloys

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ABSTRACT

Conventional arc-melting and casting is the most widely used synthesis method of high-entropy alloys (HEAs). However, the extremely high melting temperature and repetitious melting processes cause the evaporation of some constituent elements with a low melting temperature, resulting in inaccuracy of composition. In this work, *in-situ* high throughput synthesis of FeCoNiCrCuAl_x was carried out in the transmission electron microscope. The dynamic melting process of FeCoNiCrCu with Al was recorded, and the composition of FeCoNiCrCuAl_x was examined by an energy dispersive spectrometer. The *in-situ* high throughput method provides a novel way to prepare HEA samples efficiently.

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Recently, high-entropy alloys (HEAs) have drawn increasing attention due to their unique characteristics and promising properties. HEAs were firstly defined by Yeh et al. as solid solution alloys that contained multiple principal elements in equimolar or near equimolar ratios (at.%) [1]. Four core effects have been proposed in HEAs: high-entropy effect, severe lattice-distortion effect, sluggish diffusion effect and cocktail effect [2]. In the earlier stages, amazing performances of HEAs were claimed to derive from the four core effects of HEAs. However, as the research deepened, different perspectives of the core effects began to emerge. Some researchers claimed that no solid evidence could be found to support the significance of the four core effect. There was no sufficient evidence existing to establish the strain in the lattice of HEAs. Owen et al. assessed the lattice strain in the CrMnFeCoNi HEA using neutron radiation but no obvious difference was found between the HEA and other five compositionally simpler materials within the same system, which was inconsistent with the lattice-distortion effect [3]. Miracle and Senkov reported that the diffusion kinetics of Ni in FeCoNiCrMn0.5 was even faster than that in conventional materials [4]. It has been reported that generally the face-centered cubic (FCC)-structured HEAs showed low strength and high plasticity at room temperature [5], while the body-centered cubic (BCC)-structured HEAs exhibited the opposite completely [6]. However, Wu et al. successfully fabricated HfNbTiZr with single BCC structure, presenting a fracture stress of 969 MPa and a plastic strain as high as 14.9% [7]. Ye et al. revealed the non-symmetric residual field which resulted from atomic scale lattice distortion through the first principles calculations to illustrate the plasticity enhancement in HEAs [8]. In addition to revealing the characteristics of HEAs, high attention was focused on explaining

their excellent properties by studying their microstructures and deformation behaviours.

Based on a traditional understanding of alloys, multiple principal elements commonly result in complex intermetallic compounds, which would lead to brittleness in performance and difficulty in analysis. It is widely accepted that high mixing entropy as well as proper atomic-size difference and enthalpy of mixing are important issues for HEAs to form single phase solid solution [7,9–11]. So careful selection of compositions was required to satisfy the HEA-formation criteria to form solid solutions instead of intermetallic compounds. To date, most of the existing HEAs were identified through trial-and-error experiments because there was no phase diagram on quaternary and higher systems. So, it is of great importance to efficiently predict whether the selected elements could form HEAs or not. Kinds of research have been carried out to study the theoretical predictions for HEAs. He et al. suggested considering the properties of the individual elements, the underlying interatomic correlations, the estimated alloy melting temperature and even the processing temperature of the alloy when selecting the composition of HEAs [12]. Zhang et al. [13–15] concluded that high entropy of mixing ($\Delta S_{\text{mix}} > 1.61R$), low atomic size difference ($\delta < 4.6\%$), and near zero of the absolute value of the enthalpy of mixing ($-2.685\delta - 2.54 < H_{\text{mix}} < -1.28\delta + 5.44$) could facilitate the formation of HEAs. Guo et al. [16] suggested using the valence electron concentration (VEC) to predict the BCC and FCC-structured solid solutions of HEAs. For the BCC-structured solid solution, VEC should be lower than 6.8, while for FCC, VEC should be higher than 8. Experimentally preparing HEAs is the key to verify those theoretical predictions and is the precondition for studies of HEAs' properties. HEAs are mainly prepared through traditional arc-melting and casting method. To be more specific, Yeh et al. [1] prepared the CuCoNiCrAlFe alloys by arc-melting the constituent elements at a current of 500 A in a cold copper hearth

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for at least five times to improve chemical homogeneity. By this method, the composition of HEAs can be adjusted easily. However, for elements with a low melting temperature or low vapor pressure such as Mn, Zn and Mg, the co-melting of them and other elements with high melting temperatures may cause inaccuracy in composition due to the evaporation. Mechanical alloying (MA) is another common way to prepare HEAs with good homogeneity [17]. Varalakshmi et al. [18,19] successfully prepared CuNiCoZnAlTi alloy by MA. However, the MA method seemed to be inefficient since that the milling process took nearly 20 h [19].

In this work, an *in-situ* high throughput method was developed to prepare HEAs, which provided an entirely new and efficient way to prepare high-quality micro-samples. FeCoNiCrCu bulk samples were firstly fabricated into rods with a square section of 0.25 mm × 0.25 mm by wire electrical-discharge machining followed with mechanical polishing. Afterwards, electrolytic corrosion was applied to the middle of the rods to produce a finer part with a diameter of around 20 μm. Then two ends of the rod were stretched in opposite directions until the middle part fractured to produce nano-sized sharp tips on the fracture surface. Al wire (99.99% in purity, φ0.25 mm) was electrolytically etched and stretched to produce nano-sized tips similarly. The *in-situ* melting was conducted in a transmission electron microscope (TEM, JEM-2100F) equipped with an energy dispersive spectrometer (EDS, Oxford). The *in-situ* process was recorded by a Gatan 832 CCD with a rate of 2 frames/s. The HEA rod and Al rod were assembled on each end of a Nanofactory holder, and a voltage (3–5 V) was pre-applied to the two ends (Fig. 1). When the two rods contacted, a current path was formed, and the resulting Joule heat melted both the nano-sized HEA tip and Al tip. Once the voltage was withdrawn, the melted sample would rapidly solidify to form HEA with six elements (FeCoNiCrCuAl_x).

The typical *in-situ* melting process of nanotips A1 and H1 marked in Fig. 1 was recorded in Supplemental Movie S1, and key snapshots of S1 were shown in Fig. 2. Original nano-sized tips were like a triangle, with a width of about 20–50 nm. The upper side was the HEA, and the opposite was the Al. When the Al tip contacted with the HEA tip, suddenly formed electrical current would make both tips burst back to respective internal. The irregular triangle tips turned into two semicircles due to the surface tension (Fig. 2a). Then we gently moved the Al tip towards the HEA and made contact, resulting Joule heat would melt both tips, and a joint was formed between the Al and HEA tips (Fig. 2b). When we carefully drew back the Al tip with a step of 0.1 nm, the joint deformed, necked and gradually fractured to form new tips (Fig. 2c). The above process could be repeated several times to assure the uniformity of composition. The middle part of the bridge was supposed to be FeCoNiCrCuAl_x. Fig. 2d shows the EDS spectrum of the white circle region in Fig. 2b. The contents of each element were determined to be 13.1 at.% Al, 17.3 at.% Fe, 17.5 at.% Co, 17.2 at.% Ni, 17.6 at.% Cr and 17.3 at.% Cu. The chemical composition of the joint formed from A1 and H1 nanotips is close to FeCoNiCrCuAl_{0.75}. A high-resolution TEM (HRTEM) image of the joint showing typical FCC lattice under [011] zone is given in Fig. 2e. Both the HRTEM image and electron diffraction patterns confirm that the FeCoNiCrCuAl_{0.75} has the FCC structure. It was reported by Tang et al. [20] that when the Al content in FeCoNiCrCuAl_x HEA was less than $x = 0.8$, the HEA was composed of a single FCC

structure. The results in Fig. 2e are consistent with the above report. According to the HRTEM image, the interplanar spacing of (111) was measured to be about 0.216 nm, and that of (200) was about 0.196 nm. Those data are in agreement with the conclusion of Tong et al. [21] that the lattice constant of FCC FeCoNiCrCuAl_{0.7} was about 3.59 nm. Based on the chemical composition and lattice structure analysis, it can be concluded that a FCC-structured HEA with six elements was successfully synthesized by the nano-melting method.

A2 and H2 nanotips were similarly melted to obtain a joint. Then the A2 nanotip was drawn back, and the joint was broken. Part of the joint was remained on the side of H2 to form a new nanotip (A2H2). The fresh-formed A2H2 nanotip was then melted with A3 nanotip to form a joint A2H2/A3. The fabrication of the joint A2H2/A3 is schematically illustrated in Fig. 3a. Fig. 3b gives the EDS spectrum of the joint A2H2/A3. The contents of each element were determined to be 17.4 at.% Al, 16.4 at.% Fe, 16.7 at.% Co, 16.3 at.% Ni, 16.7 at.% Cr and 16.5 at.% Cu. The chemical composition of the joint A2H2/A3 is close to FeCoNiCrCuAl_{1.05}. Fig. 3c shows the HRTEM image of the joint A2H2/A3, which presents a typical square lattice structure. Assuming this area to be a FCC phase, the interplanar spacings (d) of (200) and (220) were measured to be about 0.21 and 0.15 nm, which are close to the (200) and (220) of pure Al ($d_{(200)Al} = 0.203$ nm, $d_{(220)Al} = 0.143$ nm). Assuming this area to be a BCC phase, the interplanar spacings of (110) and (200) were measured to be about 0.21 and 0.15 nm, which are close to the (110) and (200) of BCC-structured FeCoNiCrCuAl_x. The composition result in Fig. 3b excludes the assumption of pure Al. According to the research of Tang et al. [20], FeCoNiCrCuAl_{1.05} presented a mix of FCC and BCC phase. The lattice parameters of the BCC phase in FeCoNiCrCuAl_{1.0} was reported to be about 0.287 nm. So the corresponding interplanar spacings of (110) and (200) should be 0.203 and 0.143 nm, which are in good agreement with the experimental results.

Two typical *in-situ* melting situations were presented above. In the first one, Al was melted into the FeCoNiCrCu HEA, which led to a single FCC phase with a composition of FeCoNiCrCuAl_{0.75}. In the second trial, Al was further melted into the FeCoNiCrCuAl_{0.75} to produce the FeCoNiCrCuAl_{1.05}, which contained both FCC and BCC phase. The composition and lattice structure in both trials were consistent with previous researches [20,21]. All these results firmly prove that the *in-situ* melting method is viable and of great convenience to produce nano-scaled HEA with various compositions. A typical weight of raw materials required is 10–20 g in a traditional arc-melting process and is 1–3 g in MA process. However, the size of material required for the *in-situ* nano-melting is about 40 nm × 50 nm, corresponding to a weight of 1.7×10^{-16} g (for Al) or 4.9×10^{-16} g (for FeCoNiCrCu). A power of 5 kW and a melting period of 2 min × 5 times were used in traditional arc-melting, resulting in an energy input of 3 MJ ignoring the energy requirement of assistant systems such as cooling system and vacuum system. The applied voltage was 3 V, the melting current was 1 μA and the melting period was <1 s during the *in-situ* nano-melting process. Therefore, the energy input for five-times nano-melting was about 15 μJ ignoring the energy requirement of the assistant systems such as TEM. The outstanding material and energy savings of the *in-situ* nano-melting provide the possibility of high throughput synthesis of HEAs.

The advantage of the *in-situ* nano-melting method is further outlined by the convenient on-line characterizations. Once a joint is obtained by melting two tips, the chemical composition could be quickly determined by the *in-situ* EDS and the structural information could be analyzed by *in-situ* HRTEM and electron diffraction. In traditional synthesis methods, the prepared samples are needed to transfer to test equipment with required pre-treatments. The outstanding material and energy savings and the convenient on-line characterizations make our *in-situ* nano-melting method extremely suitable for high throughput study of HEAs and other materials.

The dynamic melting process of HEA was conducted by using *in-situ* TEM. By controlling the melting process, HEAs with different compositions could be obtained efficiently. The compositions of HEAs were

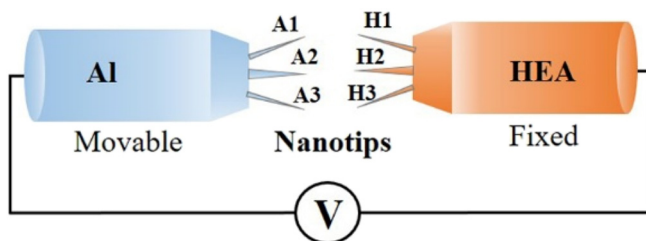


Fig. 1. Schematic illustration of the *in-situ* experimental setup.

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