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Alexander D. Dupuy , Xin Wang & Julie M. Schoenung

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ORIGINAL REPORT



Entropic phase transformation in nanocrystalline high entropy oxides

Alexander D. Dupuy , Xin Wang and Julie M. Schoenung

Department of Materials Science and Engineering, University of California, Irvine, CA, USA

ABSTRACT

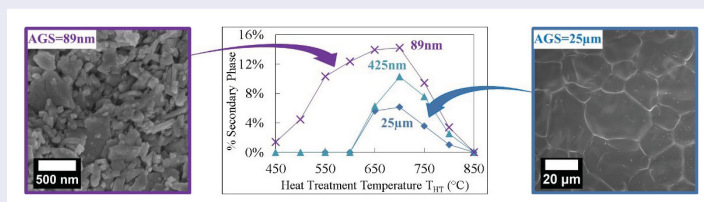
High entropy oxide (HEO) materials display a reversible entropy-driven phase transformation that gives rise to a phase state consisting of the entropic single-phase and controllable volume fractions of a secondary phase, which we call the ‘phase spectrum’. Consolidated HEO samples were prepared with grain sizes spanning several orders of magnitude and were heat treated to demonstrate the dramatic effect that grain size has on controlling the phase spectrum behavior. The volume fraction and morphology of the secondary phase, determined here to be a Cu-rich multicomponent tenorite phase, and the corresponding heat treatment conditions were significantly influenced by the grain size.

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spark plasma sintering (SPS);
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length-scale effects



IMPACT STATEMENT

Nanocrystalline high entropy oxides (HEOs) exhibit a wider phase transformation temperature window, as well as changes to the concentration and morphology of the secondary phase, a Cu-rich multicomponent tenorite phase.

Introduction

High-entropy stabilization has, for more than a decade, allowed metallurgists to explore the expanded compositional space available with high-entropy alloys (HEA) [1]. In 2015 Rost et al. created the first high-entropy oxide (HEO) [2], which consisted of five oxide components that formed the (Co,Cu,Mg,Ni,Zn)O solid solution with a single-phase rock salt structure. This work convincingly demonstrated the role of entropy in stabilizing this single-phase state and the ability to expand the compositional space beyond the borders of multi-phase phase diagrams in ceramic material systems. Since the publication of this work, high entropy stability has also been applied to perovskite [3] and non-oxide ceramic systems [4]. HEO materials have already begun to show promise as high performance capacitors [5], solid state electrolytes [6], and cathode materials [7].

An additional benefit of HEOs is their *reversible* entropic phase transformation. This reversibility suggests

that HEOs can be engineered to maximize the competition between an enthalpy-dominated multi-phase state and an entropy-dominated single-phase state. This principle manifests itself in the previously studied (Co,Cu,Mg,Ni,Zn)O system as the phase separation of a tenorite phase during heat treatment. Different heat treatment and quench conditions change the amount of tenorite phase separation, leading to a highly controllable phase state. (Co,Cu,Mg,Ni,Zn)O, however, has thus far been demonstrated to exhibit a relatively narrow temperature range (650–850°C) within which the phase state can be controlled [2]. Below this temperature window the phase cannot be altered, while temperatures above this window produce only the single-phase state. Heat treatments performed within this temperature window produce a range of phase heterogeneity between the single-phase state and the maximum allowable inhomogeneity. We call this temperature window, and the range of phase inhomogeneity that results, the

‘phase spectrum’. This unique *reversible* phase evolution should impact almost every material property; selectable phase homogeneity will provide an additional tactic in the pursuit of optimal material properties.

Sarkar et al. have shown that the single-phase state can be preserved in (Co,Cu,Mg,Ni,Zn)O powders with crystallite sizes smaller than 65 nm [8]. These HEO nanocrystals maintain the ability to reversibly transform between a single-phase and two-phase state. Recent work has shown that it is possible to improve the sinterability of (Co,Cu,Mg,Ni,Zn)O by using nanopowders synthesized from wet chemical methods [9]. Hong et al. showed that fine grain sizes can be preserved in bulk (Co,Cu,Mg,Ni,Zn)O using spark plasma sintering (SPS) [10]. The influence of grain size on the phase spectrum behavior has not, however, been explored, especially for bulk consolidated material. Here we explore the effect of grain size on the phase evolution in the (Co,Cu,Mg,Ni,Zn)O system (referred to hereafter as HEO). We show that it is possible to create primarily single-phase, fully-dense HEO samples with nanocrystalline grain sizes. Leveraging the strategies for preparing those samples, we consolidated several fully-dense HEO samples with average grain sizes (AGS) spanning several orders of magnitude. These samples were used to explore the influence of AGS on the phase spectrum behavior.

Methods

HEO powders were synthesized using conventional solid-state methods. All starting chemicals were sourced in the form of nanopowders from US Research Nanomaterials. NiO (18 nm reported particle size, 99.98 wt% purity), MgO (50 nm, 99.95%), ZnO (18 nm, 99.95%), CuO (25–55 nm, 99.95%), and CoO (50 nm, 99.7%) nanopowders were mixed in equimolar amounts using an agate mortar and pestle followed by planetary ball milling (PBM) in a Fritsch Premium 7 mill. PBM was performed at 300 rpm for 3 h using silicon nitride jars/media with the powder suspended in isopropanol. HEO powders that have only been mixed as described above are referred to here as mixed oxide (MO) powders. Some MO powders were calcined at 900°C for 20 min to form coarse-grained single-phase HEO powder and were reground in the PBM at 450 rpm for 12 h; these powders are hereafter referred to as pre-reacted (PR) powders.

Conventional sintering (CS) and SPS were used to consolidate samples from the MO and PR powders. Coarse-grained microstructures were achieved using CS in a CM Furnaces 1210BL elevator furnace at 1100°C with a hold time (t_{CS}) of 1 or 24 h. Fine-grained microstructures were achieved using a Fuji model 825S

SPS instrument with a heating rate of 200°C/min to a temperature (T_{SPS}) of 700–900°C under a pressure of 100 MPa. T_{SPS} was held for 5 min, after which the system was cooled at 50°C/min while the applied pressure was slowly reduced to zero.

A heat-soak-quench sequence was employed on each consolidated HEO sample. Heat treatments were performed using the elevator furnace at temperatures (T_{HT}) ranging from 450–850°C and a 2 h hold. The hot zone of the furnace was heated to the target temperature. The room temperature sample and elevator were then lifted into the hot zone, allowing the sample to heat rapidly. This procedure prevents the sample from spending time at lower temperatures that might convolute the phase state at the target temperature. Quenching was achieved by lowering the sample and elevator into the path of a fan blowing room temperature air.

The density of the as-consolidated samples was measured using the Archimedes method. Relative density was calculated using a theoretical density of 6.137 g/cm³ [8]. Microstructural analysis was performed using both a FEI XL-30 and a Tescan GAIA3 scanning electron microscope (SEM). Fracture surfaces were used to determine AGS. Scanning transmission electron microscopy (STEM) was performed using a JEOL JEM-2800. The STEM foil specimen was prepared with the focused ion beam (FIB) lift-out process using a FEI Quanta 3D SEM/FIB. Elemental mapping was performed in both SEM and STEM using energy dispersive X-ray spectroscopy (EDS).

X-ray diffraction (XRD) analysis was performed after each quenching step to assess the phase state. A Rigaku Ultima III diffractometer was used over the 2θ range of 30–80° (figures display 30–45° for brevity). Secondary-phase content was determined from Rietveld refinement analysis using GSAS II [11]. Structure parameters from Sarkar et al. were used as a starting point for refinement [8].

Results and discussion

The evolution of the HEO powder from an unreacted MO nanopowder mixture to a single-phase PR nanopowder is shown in Figure 1(a). XRD measurements for the MO powder display peaks from the constituent nanopowders confirming that the MO powder is an unreacted mixture of the initial five oxides. A single-phase structure is obtained after calcining the MO powder at 900°C, indicating that the reaction is complete in the PR powder. After PBM, the PR powders contain primarily individual and agglomerated nanoparticles (Figure 1(b)) and the single-phase state is maintained. These results corroborate those observed by Sarkar et al. [8], showing

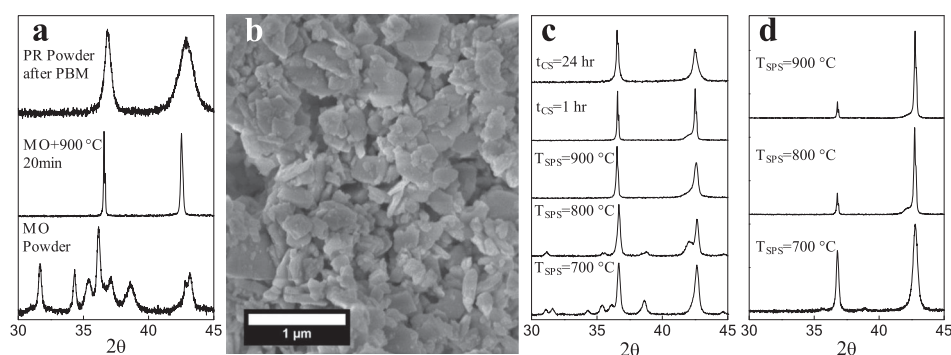


Figure 1. Synthesis and consolidation of HEO ceramics. (a) XRD patterns for PR nanopowders. (b) SEM micrograph of PR nanopowder after PBM. (c) As-sintered XRD patterns for HEO samples densified from MO powder. (d) As-sintered XRD patterns for HEO samples densified from PR powder.

that a single-phase structure can be maintained in HEO nanopowders.

In samples consolidated from MO powders, the as-sintered phase state depends on sintering temperature. The CS- and the SPS-consolidated samples processed at $T_{SPS} = 900$ °C exhibit similar XRD patterns (Figure 1(c)). The lack of extraneous peaks indicates that these samples are fully reacted and in a single-phase state. The asymmetry in the rock salt peaks can be attributed to a Jahn–Teller effect arising from the distorted coordination of the Cu atoms [12,13]. Alternatively, the samples consolidated at $T_{SPS} = 800$ °C and 700 °C exhibit secondary peaks in addition to the primary HEO structure, indicating that the solid-state reaction of these SPS-consolidated MO powders has not reached completion. Peaks from CuO and CoO can still be observed at $T_{SPS} = 800$ °C, in contrast to Hong et al., who show less intense secondary peaks at these temperatures [10]. Our still prominent secondary peaks at $T_{SPS} = 800$ °C can be attributed to our shorter SPS experiments (200 °C/min heating rate and 5 min hold time). $T_{SPS} > 800$ °C is needed for single-phase HEO samples from MO powders. However, such high temperatures are incompatible with retaining nanocrystallinity in bulk HEO samples.

Consolidating PR nanopowders yields samples with single-phase XRD patterns (Figure 1(d)). Samples processed at $T_{SPS} = 800$ and 900 °C display the single-phase pattern, while a minor amount ($< 1\%$) of secondary

(tenorite) phase is found at $T_{SPS} = 700$ °C. PR nanopowders allow consolidation of single-phase samples at lower temperatures compared to the MO powders, which require consolidation temperatures > 800 °C. It is critical that any exploration of the phase evolution begins with consolidated samples that have a primarily single-phase state. Thus, the remainder of this work focuses on the CS MO-based samples and the SPS PR-based samples that are single-phase after consolidation and prior to any subsequent heat treatment. The sample labels used in the remainder of this work, as well as the sample properties, are summarized in Table 1.

Using SPS and CS, it was possible to consolidate HEO samples with AGS values spanning several orders of magnitude (note the logarithmic scale in Figure 2(a)). The high temperatures involved in CS (1100 °C) produce samples with large AGS values (25 and 12 μm for samples CS24 and CS1, respectively). These samples also display equiaxed microstructures (Figure 2(b,c)). Alternatively, SPS-consolidated PR nanopowders yield samples with AGS values spanning three orders of magnitude. Samples SPS900 and SPS800 exhibit an AGS of 2.4 μm (Figure 2(d)) and 425 nm (Figure 2(e)), respectively. The smallest AGS in this study was 89 nm, achieved from sintering the PR powders at $T_{SPS} = 700$ °C (sample SPS700), which is 400 °C lower than what was required for full consolidation of single-phase material with CS. Such low sintering temperatures allow the sample to retain

Table 1. Summary of the sintering conditions, average grain size (AGS) and relative density of the single-phase consolidated samples.

Label	Powder	Sintering technique	Sintering temperature (°C)	Sintering time	AGS (μm)	Relative density
CS24	MO	CS	1100	24 h	25 ± 11	99.4%
CS1	MO	CS	1100	1 h	12 ± 4.8	98.6%
SPS900	PR	SPS	900	5 min	2.4 ± 1.2	99.9%
SPS800	PR	SPS	800	5 min	0.43 ± 0.22	99.9%
SPS700	PR	SPS	700	5 min	0.089 ± 0.066	98.9%

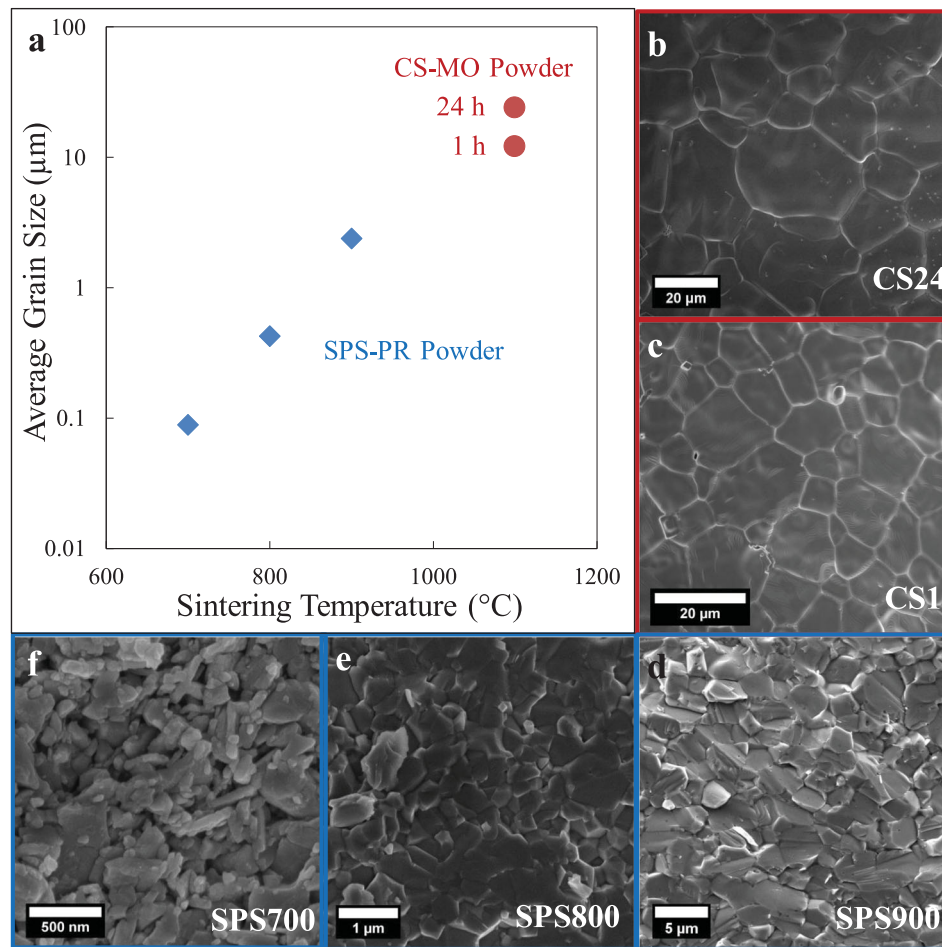


Figure 2. Role of sintering conditions on grain size. (a) AGS vs sintering temperature for CS-MO-based samples and SPS-PR-based samples (note the logarithmic scale). (b–c) Fracture surface micrographs of MO-based samples, sintered at 1100°C for: (b) $t_{CS} = 24$ h, and (c) $t_{CS} = 1$ h. (d–f) Fracture surface micrographs of PR-based samples SPS-consolidated for 5 min at: (d) $T_{SPS} = 900^{\circ}\text{C}$, (e) $T_{SPS} = 800^{\circ}\text{C}$, and (f) $T_{SPS} = 700^{\circ}\text{C}$.

the original morphology found in the PR nanopowders (Figure 2(f)). All the consolidated samples have relative densities $> 98\%$, allowing the AGS dependence of the phase spectrum to be explored independent of porosity.

The phase evolution of the coarse-grained sample CS24 (Figure 3(a)) indicates that no secondary-phase peaks appear after heat treating at $T_{HT} = 550^{\circ}\text{C}$ for 2 h. Some secondary phase emerges after heat treating at $T_{HT} = 650^{\circ}\text{C}$ for 2 h, marking the beginning of the phase spectrum for sample CS24. Higher T_{HT} values yield a two-phase state until $T_{HT} = 850^{\circ}\text{C}$, when only the single-phase structure is present, indicating the boundary of the phase spectrum. Samples CS1, SPS900, and SPS800 have phase spectra with similar temperature boundaries (summarized in Table 2). In contrast, sample SPS700 displays a different phase evolution (Figure 3(b)): secondary-phase peaks can be seen at T_{HT} as low as $T_{HT} = 450^{\circ}\text{C}$. These secondary-phase peaks remain visible until they disappear at $T_{HT} = 850^{\circ}\text{C}$.

The phase evolution can be quantitatively assessed using the Rietveld refinement method (Figure 3(d)). In the CS samples, secondary phases cannot be detected at $T_{HT} \leq 600^{\circ}\text{C}$, as confirmed by the refinement failing to converge when a tenorite phase is incorporated into the model. The fraction of secondary phase increases in both CS samples as T_{HT} increases, reaching a peak at $T_{HT} = 700^{\circ}\text{C}$. Further increases in T_{HT} lead to a decrease in secondary-phase content until $T_{HT} = 850^{\circ}\text{C}$ when the secondary phase disappears. Both coarse-grained samples (C24 and CS1) demonstrate similar phase evolution behavior despite the roughly factor-of-two difference in AGS (25 μm vs 12 μm), indicating that the phase spectrum manifests similarly in materials with an AGS in the same order of magnitude.

The quantitative phase evolution of the SPS PR-based samples highlights that SPS900 and SPS800 (AGS = 2.4 μm and 425 nm, respectively) behave similarly to the CS samples. In these samples, the secondary phase forms at $T_{HT} = 650^{\circ}\text{C}$, is maximized

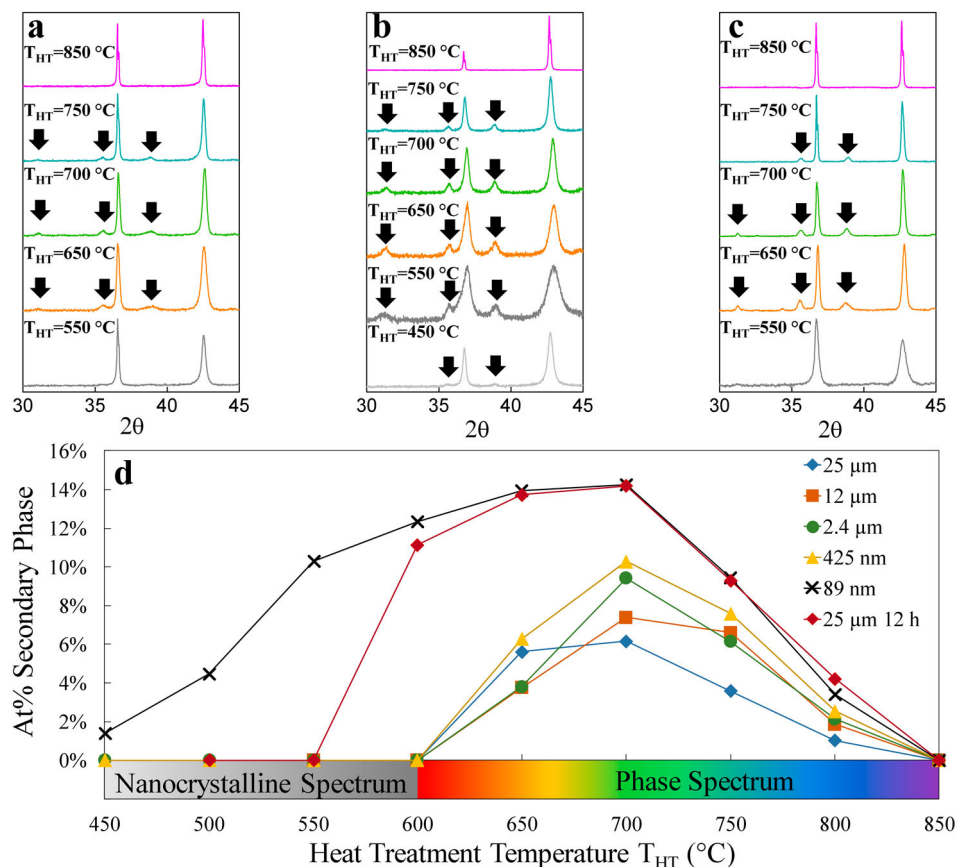


Figure 3. Role of grain size on phase spectrum behavior. (a–b) XRD patterns taken after heat treatments at the designated T_{HT} . (a) CS24 (AGS = 25 μ m), and (b) SPS700 (AGS = 89 nm) patterns after 2 h heat treatments. (c) CS24 patterns after 12 h heat treatments. Arrows indicate the tenorite phase. (d) Atomic percent (at%) secondary phase (tenorite) vs T_{HT} . All heat treatments were performed for 2 h except for the data set labeled '25 μ m 12 h'. As-consolidated AGS values are noted in the legend. The inset in the x-axis represents the phase spectrum and its relationship to T_{HT} . The phase spectrum is color coded to the XRD patterns (a–c).

Table 2. Atomic percent (at%) secondary phase (tenorite) achieved in the consolidated samples after heat treatment at T_{HT} for 2 h, except sample CS-24-12 h, which was heat treated for 12 h.

	Heat treatment temperature, T _{HT} (°C)								
	450	500	550	600	650	700	750	800	850
CS24 (25 μm)	0%	0%	0%	0%	5.6%	6.2%	3.6%	1.0%	0%
CS1 (12 μm)	0%	0%	0%	0%	3.8%	7.4%	6.6%	1.8%	0%
SPS900 (2.4 μm)	0%	0%	0%	0%	3.8%	9.4%	6.1%	2.1%	0%
SPS800 (425 nm)	0%	0%	0%	0%	6.3%	10.3%	7.6%	2.5%	0%
SPS700 (89 nm)	1.4%	4.4%	10.3%	12.3%	14.0%	14.3%	9.5%	3.4%	0%
CS24-12 h (25 μm)	0%	0%	0%	11%	13.7%	14.2%	9.3%	4.2%	0%

A gray cell indicates a single-phase state while a white cell indicates a two-phase state.

at $T_{HT} = 700^\circ\text{C}$, and disappears at $T_{HT} = 850^\circ\text{C}$. In contrast, secondary-phase formation begins in sample SPS700 (AGS = 89 nm) at lower T_{HT} . The presence of the secondary phase can be seen even at $T_{HT} = 450^\circ\text{C}$. Higher T_{HT} results in an increase in secondary-phase content until $T_{HT} = 700^\circ\text{C}$ when the maximum amount is reached. Samples with larger AGS values require $T_{HT} = 650^\circ\text{C}$ for 2 h before phase separation occurs. Nanocrystallinity shifts the phase spectrum to lower temperatures. The maximum amount of secondary phase increases with decreasing AGS under

identical heat treatments. AGS influences both the temperature required and the amount of secondary phase formed during heat treatment of these HEOs.

An additional experiment was performed to assess the role of heat treatment time on the phase spectrum behavior. A duplicate of sample CS24 was prepared and then heat treated from 450–850°C in 50°C increments for 12 h (instead of 2 h) at each temperature increment. XRD patterns were collected after quenching. Unlike previous phase evolution experiments, this sample was restored to the single-phase state between each heat treatment step

by heat treating the sample at 1000°C for 12 h and then quenching to room temperature. Resetting the phase state and heat treating for longer times should allow the sample to reach an equilibrium phase state at that temperature. This experiment was not performed on nanocrystalline samples due to the equilibrium phase evolution being convoluted by grain growth.

The 12 h heat treatment experiments show that heat treatment time influences the secondary-phase formation (Figure 3(c,d)). Phase separation appears during this experiment at and above $T_{HT} = 600^\circ\text{C}$ for 12 h. As T_{HT} is increased, there is initially an increase in secondary-phase content to 13.7at% at 650°C until it reaches a maximum of 14.2at% at 700°C. Further increases in T_{HT} result in a decrease in secondary-phase content until the single-phase state is achieved at 850°C.

The role of kinetics can be seen by comparing the 2 and 12 h heat treatment phase evolution in the 25 μm samples (CS24 and CS24-12 h). Secondary-phase peaks are not observed after $T_{HT} = 600^\circ\text{C}$ for 2 h. Longer heat treatment times are necessary to yield the two-phase state at this T_{HT} . Additionally, longer heat treatment times increase the amount of secondary phase at all temperatures encompassing the phase spectrum. The role of kinetics can also be observed in the nanocrystalline sample (SPS700). $T_{HT} = 700^\circ\text{C}$ for 2 h produces 14.3at% secondary-phase content, the highest amount reported in this study. Alternatively, due to the short sintering

time (5 min), the as-sintered state for SPS700 contains < 1at% secondary phase even though it is sintered at $T_{SPS} = 700^\circ\text{C}$. These examples indicate that heat treatment time can be used to adjust the behavior of the phase spectrum, even in samples with coarse AGS values.

The impact of AGS on phase spectrum behavior is particularly visible when comparing the phase evolution in the 89 nm AGS sample (SPS700) to the 25 μm AGS samples (CS24 and CS24-12 h). $T_{HT} = 700^\circ\text{C}$ for 2 h is sufficient to reach 14.3at% secondary-phase content in the nanocrystalline sample, while 12 h at 700°C is required for samples with AGS = 25 μm , implying that AGS influences the phase separation kinetics. However, an increase in the secondary-phase content is observed in the nanocrystalline sample after heat treating at $T_{HT} = 450^\circ\text{C}$ for only 2 h. Even with 12 h heat treatments, the sample with AGS = 25 μm does not show any secondary phase until temperatures of at least 600°C, indicating that the influence of AGS on the phase spectrum behavior cannot be attributed solely to kinetics. Instead, some additional mechanisms must be involved.

The morphology of the secondary phase in the coarse-grained samples was examined using a polished surface of CS24-12 h after being heat treated at $T_{HT} = 700^\circ\text{C}$. SEM microscopy reveals that the secondary phase consists of particle and needle-like structures that emerge in both the grain boundaries and grain interiors (Figure 4(a)). Low voltage EDS [14] (3 kV accelerating voltage)

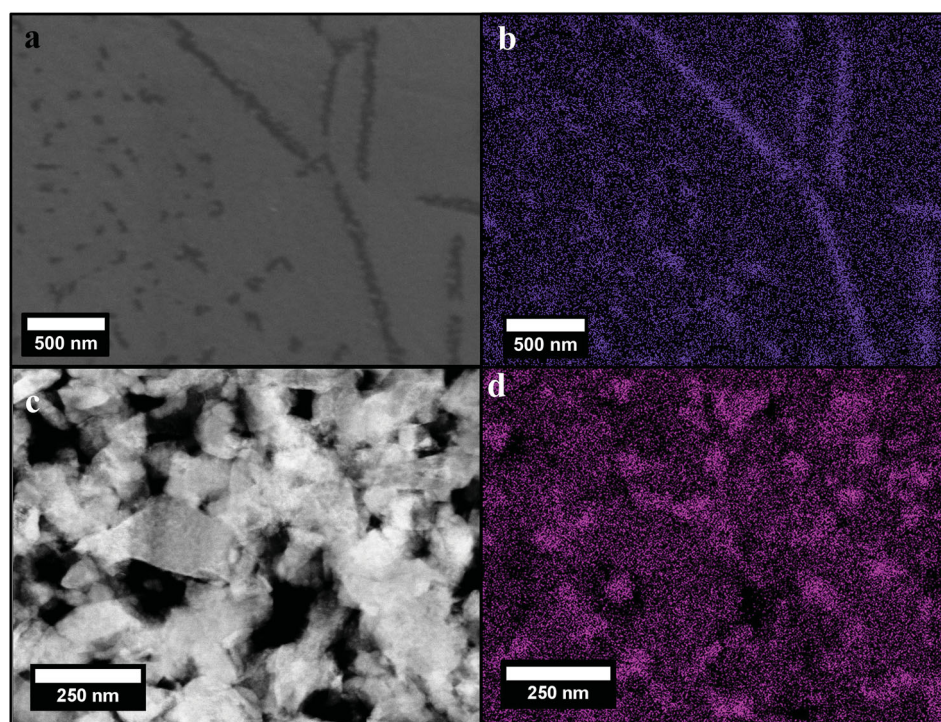


Figure 4. Morphology of the secondary phase. (a) SEM micrograph of CS24 heat treated at 700°C for 12 h and (b) the corresponding EDS map for Cu. (c) STEM micrograph of SPS700 after sequentially heat treating from 450–550°C in 2 h increments, and (d) the corresponding EDS map for Cu.

confirms that these structures are Cu-rich (Figure 4(b)). STEM was performed on a FIBed foil of SPS700 after being sequentially heat treated at $T_{HT} = 450, 500,$ and 550°C for 2 h at each temperature. Unlike for the coarse-grained samples, the secondary phase cannot be immediately observed in the STEM images (Figure 4(c)), yet EDS analysis reveals that Cu-rich grains are distributed randomly throughout the sample (Figure 4(d)). The primary-phase and Cu-rich grains are of similar size and are indistinguishable from one another without the use of EDS. Furthermore, the EDS analysis shows that the other elements are deficient, but not absent, from these Cu-rich regions (not shown), which indicates that the secondary phase is not pure CuO, but instead a Cu-rich multicomponent tenorite phase.

The secondary phase is ubiquitous in the grain boundaries of the two-phase coarse-grained sample, consistent with the modest change in phase evolution in samples with $AGS = 25\ \mu\text{m}$ to $425\ \text{nm}$: as AGS decreases the grain boundary volume of the sample increases, providing more grain boundary for the secondary phase to occupy under the same heat treatment conditions. Alternatively, secondary-phase morphologies observed in the coarse-grained sample are not observed in the nanocrystalline sample—rather, individual grains of secondary phase are observed instead—indicating that the stable morphology of the secondary phase changes as a function of length scale. The current results suggest that this transition occurs when the AGS is similar in size to the secondary-phase features, resulting in the secondary phase forming primarily from the grain boundary. As the grain boundary will be the preferential site for phase separation, increasing the grain boundary volume will decrease the required temperature for secondary-phase formation. We therefore attribute the change in phase evolution behavior to the high grain boundary volume found in the nanocrystalline HEO, which will enhance the diffusion kinetics and alter the secondary-phase morphology. Our observed length-scale dependent phase behavior exhibits similarities to the precipitation behavior in some nanocrystalline HEA materials [15]. Further work is ongoing to explore these length-scale effects in more detail.

Conclusions

Single-phase fully-dense HEO samples with AGS values spanning several orders of magnitude were prepared using single-phase nanopowders synthesized through heat treatment and PBM, followed by consolidation using CS and SPS, and were used to investigate the influence of AGS on the phase spectrum behavior. AGS dramatically influenced the phase spectrum behavior, particularly at

nanocrystalline grain sizes: smaller grain sizes increased the total amount of secondary phase formed during the phase evolution and decreased the transformation temperature. The secondary phase, which was determined here to be a Cu-rich multicomponent tenorite phase, was observed to change morphology with grain size. These findings suggest that HEO ceramics can be engineered with pre-specified phase fractions and morphologies, thereby controlling microstructure and ultimately behavior.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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ORCID

Alexander D. Dupuy  <http://orcid.org/0000-0002-7405-5341>

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