Microstructure Evolution of (MgCoNiZnCu)O High Entropy Oxides Using Ceramic Injection Molding

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Research Article

Keywords: high entropy oxides, rock-salt structure, near net shaping process, cost-effective

Posted Date: September 15th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-855939/v1>

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Abstract

Near net shaping ceramic injection molding process of (MgCoNiZnCu)O high entropy oxides were conducted using commercial precursor oxide powders. Through ball milling, internal mixing, injection molding, solvent and thermal debinding as well as final sintering process, the ceramic products would be obtained with little machining. Compacts prepared are single rock-salt phase based on XRD and EDS Mapping results. Meanwhile, with the increasing of sintering temperature from 900 °C to 1050 °C, particle diffusion rate and densification of samples becomes faster, which finally results relative density and fractured strength of sintered compacts reaching the highest (90.47 % and 77.98 MPa, respectively) in current work. The successfully synthesis of (MgCoNiZnCu)O through ceramic injection molding illustrates this near net shaping process could be a promising route for preparation of high entropy oxides.

Highlights

A cost effective near net shaping method for (MgCoNiZnCu)O high entropy oxides was proposed.

(MgCoNiZnCu)O samples synthesized are single rock-salt phase with homogeneous microstructure.

The relative density of ceramic injection molding compacts reaches 90.47%.

Introduction

The ‘high entropy’ material was first introduced by Yeh et al for described high entropy alloys (HEA) which is composed of five or more metal elements in equimolar or near equimolar ratios[1]. An N-species material system with composition (x_i) has ideal configurational entropy S [2]:

$$S = -R \sum_{i=1}^N x_i \log(x_i) \quad (1)$$

Maximum S_{max} is acquired at stoichiometric amounts, as $x_i = 1/N$ for each i , hence:

$$S_{max} = R \log (N) \quad (2)$$

In regard to a high entropy system, it is well known that configurational entropy is always not less than $1.61R$ [3].

Rost et al. extended the HEA concept to the field of ceramics and successfully synthesized a rock-salt structure (MgCoNiZnCu)O high entropy oxide (HEO) in 2015[2]. The HEO rock-salt phase has two different kinds of sublattices: the oxygen particles occupy the sites of face centered cubic lattice while the five kinds of cations locate at the octahedral gaps of the oxygen atoms randomly and uniformly[4,5]. Since then, HEO especially (MgCoNiZnCu)O has been thoroughly studied because of colossal dielectric constant[6], exceptional lithium-ion conductivity[7], excellent magnetic properties[8] and catalytic

performance[9]. The incorporation of different metal cations in a single lattice structure, their possible synergistic effects, and the larger configurational entropy contribute to such multifunctional properties for this type of materials. Besides, much attention has been focused on synthesis of HEO and its derivatives[10], with methods including solid-state reaction[6], nebulized spray pyrolysis[4], flame spray pyrolysis[4], co-precipitation[11] and solution combustion method[12].

Among the large quantity of existing synthesis process for advanced ceramics, it is worth noting that ceramic injection molding (CIM) could overcome limitations of conventional procedures due to a series of outstanding advantages. As a cost-effective near net shaping process, CIM attracts wide attention in recent years which could manufacture small, complex shaped, high dimensional precision ceramic compacts in enormous quantities[13–15]. This technology is usually comprised of four basic stages: compounding of feedstock, injection molding, debinding and sintering[16,17]. Feedstock of CIM usually consists of organic binders and ceramic powders. The binder system is a complex mixture composed of several components which is strictly selected to facilitate well injection properties and can be easily removed from green parts[18]. Binders used in CIM mainly consist of three functional components including: lubricants providing rheological properties for feedstock, macromolecular binders maintaining the shape integrity of green parts and debound compacts, as well as surfactants improving compatibility between ceramic powders and other organic binders[19]. CIM technology was used to fabricate a series of ceramic materials as follows: Al_2O_3 [20,21], ZrO_2 [19,22], CaO [18], SiO_2 [23], MgAl_2O_4 [24,25], SiC [26], B_4C [27], AlN [13], Si_3N_4 [28] and ZrB_2 [29] et al. Through this near net shaping CIM process, a large quantity of ceramic parts have been synthesized in recent years. Qin et al. [13] reported the CIM of complex shaped AlN ceramic with high thermal conductivity and successfully synthesized AlN heat sinks. Gromada et al. [30] have obtained materials allowed for the formation of ceramic cores with complicated shapes and high dimensional accuracy. While Hu et al. [20] fabricated a series of translucent alumina ceramics as prefabricated dental post, orthodontic dental ceramic bracket and relatively large size ceramic bowls using surface modified alumina powders.

In accordance with the best of our authors' knowledge, despite the previously described superiority of CIM technology, it has been never used to synthesize multi-components high entropy materials especially $(\text{MgCoNiZnCu})\text{O}$ HEO. In light of this aspect, a single rock-salt structure $(\text{MgCoNiZnCu})\text{O}$ was successfully synthesized for the first time using near net shaping CIM technology in present study. Besides, the Microstructure evolution of $(\text{MgCoNiZnCu})\text{O}$ was systematically discussed to provide process guidance for the future work about the synthesis of HEO through CIM.

Experimental

2.1 Preparation of $(\text{MgCoNiZnCu})\text{O}$

$(\text{MgCoNiZnCu})\text{O}$ HEO was prepared from MgO (99.9% purity, 2.5 μm), CoO (99.9% purity, 1 μm), NiO (99.9% purity, 1 μm), ZnO (99.9% purity, 1 μm) and CuO (99.9% purity, 1 μm) acquired from Shanghai ST-Nano Science & Technology Co., Ltd. The process scheme for synthesis of $(\text{MgCoNiZnCu})\text{O}$ by CIM is

present in Fig. 1. At the first mixing stage shown in Fig. 1, ceramic powders with stoichiometric amounts and few stearic acids (SA) in ethanol were mechanically mixed by planetary ball milling (QM-3SP4) using alumina balls and vials at 300 rpm for 6 hours. Afterward dried powders (morphology and XRD pattern were shown in Fig. S1 and Fig. S2, respectively) were mixed with organic binders (polyethylene (PE), polypropylene (PP), paraffin wax (PW) and dibutyl phthalate (DBP)) in 50 vol% powder loading using an internal mixer machine (KY-3220A-1L) to prepare feedstock on 170 °C for 45 min at 40 rpm. Secondly, at injection molding stage, green parts (5×6×42 mm) were prepared using an injection molding machine (V35-CIM) with injection temperature and pressure were 180 °C and 110 MPa, respectively. Then at debinding stage, a two stage debinding process (solvent and thermal) was used to remove binder system in green parts. Hence green parts were immersed in kerosene (nontoxic, recycled and cheap) and heated to 55 °C in a water bath for 8 hours to partially remove soluble PW. Compacts after solvent debinding were heated to 500 °C for 2 hours in a debinding furnace (QH-12-11) with heating and cooling rate of 1.5 °C/min (according to TG results of Fig. 2a) to remove remaining binders. Finally at the sintering stage, compacts were transferred to a tube furnace (GSL-1500X-OTF) for sintering at 900 (about 20 °C higher than weight loss temperature of Fig. 2c), 1000, 1050 °C (a little lower than weight loss temperature of Fig. 2e) with holding time of 6, 10, 18 hours, respectively.

2.2 Characterization and measurements

Thermogravimetric (TG) and differential scanning calorimetry (DSC) experiments about mixed powder, green part and solvent debound part were carried out using a thermogravimetric analyzer (TGA/SDTA851e, Switzerland). While crystal structure of sintered samples was characterized using X-ray diffractometer (XRD-6000, Japan) equipped with Cu K α source at 4 °/min scanning speed and 20–80 ° scanning range. Analysis of polished and fractured surface was conducted by scanning electron microscopy (SEM, SUPRA 55, Germany), while selected area was characterized by energy dispersive spectroscopy (EDS, Germany) to confirm elements distribution uniformity. Grain size of compacts was estimated from micrograph of fractured surface using Nano Measurer software. According to Archimedes' principle, bulk density of sintered pellets was measured in deionized water, while compression strength was evaluated using a universal testing machine (DNS 300, China) with a cross-head speed of 0.2 mm/min.

Results And Discussion

3.1 Organic binder

Being one of the important constituents in process of CIM, organic binders always consist of several binders: low molecular weight polymers as lubricants, macromolecular binders as backbone binders as well as a small amount of surfactant[16,22]. As a surfactant, SA used in this work has both functional group anchoring to the powder surface and the carbon chain dissolving in the binders[21], hence could improve the compatibility between binders and oxide powders. During the planetary ball milling progress, the SA has been coated on the surface of oxide powders[22], and furtherly make the organic binders tightly coated on the surface of the modified oxide powders after internal mixing process. While the

lubricants (PW and DBP in this work) could improve fluidity of feedstock and enhance the wettability between organic binders and mixed powders. The lubricants also endow feedstock enough rheological properties during the injection stage for better molding abilities of complex shaped green parts. Besides, the backbone binders (PE and PP) give mechanical strength to green compacts as well as pellets after solvent debinding to maintain their shapes. Though the crucial function of organic binders at the injection and debinding stage, it is harmful at the sintering stage. Hence the combination of solvent and thermal debinding process will remove the binder system from the green parts rapidly and avoid defects. Besides, thermal properties were analyzed and evaluated through TG and DSC experiments for debinding process to accelerate the removal rate and eliminate crack defects[31].

TG results present three stages of weight loss from 150 to 1200 °C, data of DSC also show three stages in similar temperature range. Firstly, greatest weight loss occurs between 210 to 480 °C (present in Fig. 2a) due to the removal of organic binders. Detailed analysis can be gained from the DSC results of Fig. 2b as follows: the first peak from 210 to 240 °C shows decomposition of low molecular weight DBP and PW binders (mainly the lubricants), the removal temperature of SA reaches 280 °C due to great affinity between the surfactant SA and mixed powders, and peaks from 300 to 480 °C display the elimination of backbone binders PE and PP whose melting point is higher[16]. Therefore in the process of thermal debinding, the slow heating rate of 1.5 °C/min was adopted in order to maintain the complete shape and defect free of the CIM compacts. It should be stated that the weight loss of mixed powder is owing to the SA introduced from planetary ball milling for the effect of surface modification. The formation of single rock-salt solid solution high entropy structure locates at 690–880 °C explains weight loss of mixed powder, green part as well as solvent debound part shown in Fig. 2c. And from this it can be concluded that binder system was completely removed from the compacts at the first weight loss stage. Considering the former discussion, the lowest sintering temperature (locates at 900 °C) of this work is a little higher than the former temperature range (690–880 °C). The weight loss from 1100 to 1200 °C in Fig. 2d features the elimination of CuO, so the highest sintering temperature (set as 1050 °C) is lower than 1100 °C in this work.

3.2 Analysis of green and debound parts

The quality of green and debound parts will influence the quality of the final sintered CIM parts, hence the morphology of green and solvent debound parts was characterized and systematically analyzed for the purpose of defect free final parts. Figure 3(a-c) shows the surface and fractured micrograph of CIM green parts, respectively. It suggests that green parts are tightly packed by uniformly distributed ceramic powers fully surrounded by organic binders. Figure 3c presents a large quantity of fibrous binders of the fractured morphology, which is mainly caused by the elongation of organic binders in the process of fracture. Figure 3(d-f) responds to images of solvent debound samples. After partly removal of soluble PW, some pore channels were observed in compacts when compare Fig. 3d with Fig. 3a, and it could serve as escape paths for decomposed gas during subsequent thermal debinding for backbone binders[32]. After solvent debinding, there were about 10% solvent removable binders remaining in compacts except backbone binders, then subsequent thermal debinding would remove the remaining organic binders.

Finally, a sintering operation according to the parameters present in the former experimental process of this article is carried out on the debound parts to achieve the required physical and mechanical properties[33].

3.3 Morphologies and Microstructure evolution

After the preparation of sintered CIM compacts, the XRD and SEM tests are conducted to confirm the formation of HEO. XRD spectra of final compacts present in Fig. 4a illustrate that (MgCoNiZnCu)O samples sintered at 900, 1000 and 1050 °C using CIM process are single phase, with all Bragg peaks can be indexed in rock-salt Fm-3m (225) space group which is consistent with the research results of Christina M. Rost[2]. Besides, when sintered at 1050 °C, SEM images of polished morphology and corresponding EDS mapping of Mg, Co, Ni, Zn, Cu and O elements shown in Fig. 4b illustrates that the distribution of metallic and nonmetallic elements is random and uniform at this micron scale. And there exists none segregation and gathering of all constituent elements confirming the chemical and microstructural homogeneity. Given the above discussion, the XRD and EDS mapping results demonstrate that single rock-salt phase (MgCoNiZnCu)O HEO has been synthesized using near net shaping CIM process.

Sintering temperature also influences densification behavior of samples except holding time (discussed about Fig. S3). SEM micrographs of fractured samples experienced different temperature are presented in Fig. 5(a-f). At 900 °C, fractured surface indicates the package of grains is loose and the connection between grains is pretty weak as shown in Fig. 5(a, b). While compressive fractured strength of this compact is only 22.29 MPa listed in Table 1 though the mean grain size is only 2.60 μm in Fig. 5g. As a matter of fact, the removal of organic binders leaves a large quantity of micro holes in compacts after the two stage debinding process, the powder loading is 50 vol% for enough formability of ceramic injection molding process, hence there are probably 50 vol% of holes in thermal debinding samples. Despite the formation of single rock-salt phase has been achieved according to the XRD result of Fig. 4a prepared at 900 °C, the densification of compacts still needs higher sintering temperature. When the temperature of 1000 °C was reached (Fig. 5(c, d)), connections between particles become stronger but there are still some holes distributing on fractured surface, while the fractured strength and mean grain size are 58.13 MPa and 3.78 μm, respectively. At the highest sintering temperature of this work (1050 °C), Fig. 5(e, f) is characterized by a dense morphology and tightly bonded grains, with relative density above 90.47%. Hence fractured strength reaches the highest value (77.98 MPa) though grains have some roughening and the mean grain size reaches 5.56 μm. With increasing of sintering temperature, diffusion rate of particles and densification of pellets become faster, finally results the relative density as well as fractured strength reaching the highest at present study.

Table 1
Physical properties of sintered compacts

Sintering Temperature (°C)	900	1000	1050
Density (g.cm ⁻³)	5.0499	5.2889	5.5821
Relative density (%)	82.72	85.01	90.47
Fracture strength (MPa)	22.29	58.13	77.98

Conclusions

Results indicate that the TG and DSC analysis illustrate the removal mechanism of organic binders during thermal debinding experiment and the defect free brown parts were gained with a shorter process time. Micrograph of green and solvent debound parts was characterized for the purpose of obtaining defect free final parts. Then a single rock-salt phase (MgCoNiZnCu)O was successfully synthesized through CIM process. The highest value of fractured strength (77.98 MPa) was achieved for (MgCoNiZnCu)O sintered at 1050 °C, with the relative density of final HEO compact reaches 90.47%. Overall, this research clearly demonstrates that CIM is a pretty promising cost effective near net shaping technique to synthesis HEO.

Declarations

CRedit authorship contribution statement

Yipeng ZHAO: Investigation, Validation, Methodology, Writing, Visualization, Review & Editing.

Guoqing CHEN: Conceptualization, Resources, Validation, Review & Editing, Supervision, Visualization, Project administration, Funding acquisition.

Hongwei LI: Investigation, Validation, Methodology, Review & Editing.

Xuesong FU: Investigation, Validation, Methodology, Supervision.

Wenlong ZHOU: Resources, Project administration, Supervision.

Acknowledgements

This work was financial supported by the National Natural Science Foundation of China [grant numbers: U1908229, 52075073], and also supported by the Fundamental Research Funds for the Central Universities [grant number: DUT20GF115].

Supplementary Material

Supplementary material associated with this article can be found in the online version at [https:// doi.org/](https://doi.org/)

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Figures

Figure 1

Schematic for preparation of (MgCoNiZnCu)O by ceramic injection molding: mixing oxide powders with organic binders, injection molding of feedstock, solvent and thermal debinding of green part, sintering of brown part.

Figure 2

Thermal analysis results of mixed powder, green part and solvent debound part: (a) TG and DTG curves at 200-500 °C, (b) DSC curves at 200-500 °C, (c) TG and DTG curves at 600-900 °C, (d) TG and DTG curves at 1050-1200 °C.

Figure 3

Morphology of SEM images: (a) surface of green part, (b) surface of green part with a higher magnitude, (c) fracture of green part, (d) surface of solvent debound part, (e) surface of solvent debound part with a higher magnitude, (f) fracture of solvent debound part.

Figure 4

(a) XRD spectra of compacts sintered at 900, 1000 and 1050 °C, (b) SEM images of polished morphology, with the corresponding EDS mapping of Mg, Co, Ni, Zn, Cu and O elements synthesized at 1050 °C.

Figure 5

Fractured micro-graph of CIM sintered compacts: (a, b) morphology synthesized at 900 °C, (c, d) morphology synthesized at 1000 °C, (e, f) morphology synthesized at 1050 °C. Grain size distribution at different sintering temperature: (g) 900 °C, (h) 1000 °C, (i) 1050 °C. It should be noted that grain size of pellets (g), (h), (i) was estimated using nano measure software from (a), (c), (e), respectively.

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