A nanocrystalline high-entropy oxide for hydrogen storage

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INTRODUCTION:

Hydrogen has been drawing attention as a potential source of energy across the world. It is a very effective energy carrier and may soon provide a solution to the growing demand for electrical energy and the depletion of fossil fuel deposits. However, a prerequisite for the widespread adoption of hydrogen as a fuel is the development of state-of-the-art materials for hydrogen technologies, including materials for hydrogen storage and transport. This necessitates the design of materials that are capable of absorbing this element and must meet several physicochemical and technical requirements, including high gravimetric and volumetric capacity, optimal kinetics of the sorption and desorption of hydrogen, and reversibility of the absorption process. None of the currently known materials meet all of required criteria to a sufficient degree.

Novel groups of materials considered for hydrogen storage include multicomponent BCC alloys stabilized via high configurational entropy, known as high-entropy alloys. These compounds have attracted considerable interest, since their physicochemical properties are unique and have not been observed for conventional alloys.

High-entropy oxides (HEOs) are another category of multicomponent materials in the group of high-entropy compounds, and can also exhibit numerous advantageous properties, be obtained by means of different methods, and have different crystal structures. Consequently, it is likely that HEOs may likewise prove to be an interesting research subject that has not yet been investigated with regard to hydrogen storage.

METHODOLOGY:

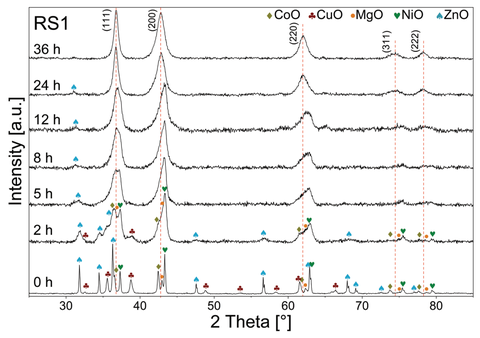
Preparation of HEOs:

Selected compositions RS1-$(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$, RS2-$(Co_{0.2}Cu_{0.2}Fe_{0.2}Mg_{0.2}Ni_{0.2})O$, RS3-$(Co_{0.2}Cu_{0.2}Mg_{0.2}Mn_{0.2}Ni_{0.2})O$, RS4-$(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$, RS5-$(Co_{0.17}Cu_{0.17}Mg_{0.17}Mn_{0.17}Ni_{0.17}Zn_{0.17})O$, RS6-$(Co_{0.17}Cu_{0.17}Fe_{0.17}Mg_{0.17}Mn_{0.17}Ni_{0.17})O$, RS7-$(Co_{0.14}Cu_{0.14}Fe_{0.14}Mg_{0.14}Mn_{0.14}Ni_{0.14}Zn_{0.14})O$ were prepared via mechanochemical synthesis (MS). Metal oxide powders – ZnO, CuO, CoO, MnO, Fe_2O_3, NiO, Co_3O_4, MgO – were used as starting materials. All series of powder mixtures were prepared using a shaker-type ball mill (SPEX 8000 Mixer/Mill), a steel vial and steel balls. The parameters of MS were: milling time – 36/72 h, ball-to-powder weight ratio (BPR) – 10:1, atmosphere – Ar. Additionally, some RS1 powder material was sintered for 5 h in static air at 1000°C to prepare additional sinters. After thermal treatment, the samples were promptly removed and air-quenched.

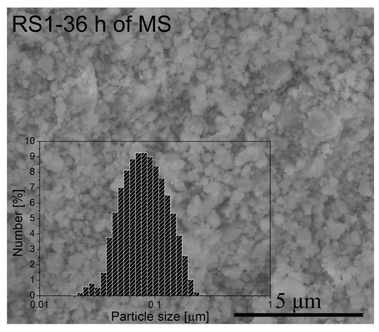
Characterization technique:

The crystal structure of the samples was investigated via XRD, using a Panalytical Empyrean diffractometer with CuKa (λ=1.54056 Å) radiation. The morphology of the samples was studied via SEM (FEI Company, NOVA NanoSEM 200). The particle size distribution was studied using dynamic light scattering (DLS) measurements performed with an SALD-7500 nano particle size analyzer (Shimadzu). The powder and sinter samples were hydrogenated under high pressure and at temperatures of 100 and 250°C using a conventional, fully automated Sievert's apparatus (Particulate Systems, HPVA 200). The chemical stability of the studied samples in an argon gas mixture with 5 vol% of hydrogen was evaluated over the temperature range of 25-600°C using a thermogravimetric analyzer (TGAQ5000 V3.17 Build 265). The heating rate was 5°C·min^{-1}.

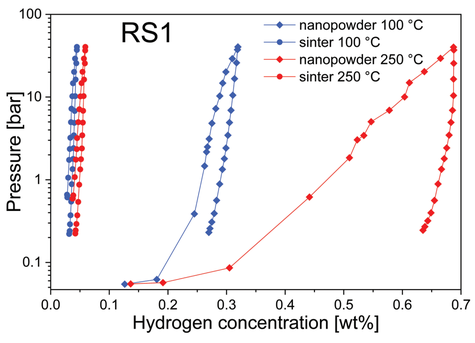
RESULTS:



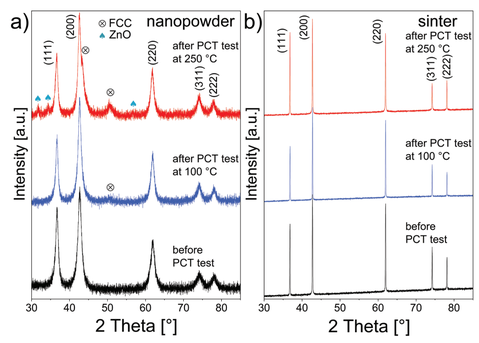
XRD diffraction patterns showing phase evolution in the RS1 sample during MS process interrupted at various breakpoints between 2 and 36 h.



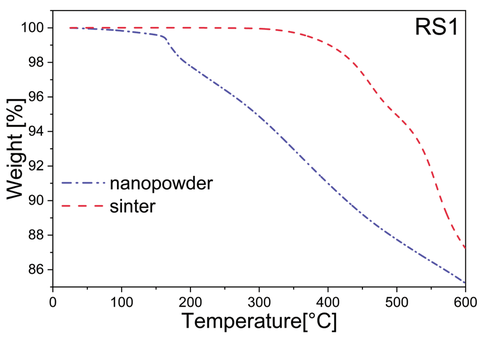
SEM image of RS1 sample after 36 h of MS. Inset: Particle size distribution.



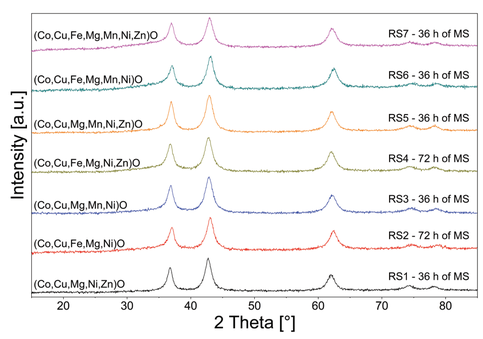
Pressure-composition-temperature (PCT) curves plotted for RS1 nanopowder and sinter samples during hydrogenation at 100 and 250°C.



XRD patterns recorded for a) RS1 nanopowder and b) RS1 sinter samples before and after PCT tests at 100 and 250°C.



Thermogravimetric analysis for RS1 nanopowder and sinter samples exposed to a hydrogen-containing atmosphere (5 vol% H_2 in Ar).



XRD diffraction patterns of HEO samples with a rock salt structure and different compositions after the MS process.

DISCUSSION:

The RS1 sample was used to optimize milling time during the MS process to obtain a single-phase high-entropy oxide with a rock salt structure. The influence of milling time on phase transitions in the studied powders was evaluated via multistage milling for times ranging from 2 to 36 h, conducted in Ar and at a BPR of 10:1. It was observed that for longer MS times the reflections originating from CuO and ZnO diminish, while the increased relative intensity of the (111), (200), (220), (311) and (222) reflections indicates that the Fm-3m phase had formed.

After 36 h of mechanochemical synthesis in argon, the RS1 sample was a nanopowder and had the form of a nanocrystalline material with groups of agglomerates less than 1 μm in size. The DLS data support the conclusions from morphological observations, indicating a unimodal, narrow size distribution, with the mean diameter values of the particles at ca. 76 nm for the RS1 nanopowder sample.

High-pressure hydrogenation of the RS1 sinter was found not to have a significant effect on the level of H_2 absorption regardless of the temperature at which the process had occurred – in both cases hydrogen concentrations changed only slightly. On the other hand, increased hydrogen content was observed for the RS1 nanopowder. In this case, hydrogen concentration was 0.32 wt% after hydrogenation at 100°C, and then increased by a factor of more than 2 – to 0.69 wt% – when exposure to hydrogen occurred at 250°C

The RS1 nanopowder that underwent hydrogenation at 100°C was found to contain a new metallic phase with an FCC structure; this can be attributed to the presence of Cu and/or Co. After increasing the hydrogenation temperature to 250°C, the intensity of reflections of the FCC phase increased significantly and a ZnO phase was also identified. This shows that in a pure hydrogen environment and at increasing temperatures, the obtained nanocrystalline HEO powder gradually decomposed into simple oxides and metals. As far as the HEO sinter is concerned, high-pressure hydrogenation did not cause any changes in its phase composition, even when the temperature and pressure during the process were 250°C and 40 bar, respectively.

In thermogravimetric (TG) analyses for the RS1 nanopowder exposed to reducing conditions and increasing temperatures up to ca. 160°C, the loss of mass was linear and the total mass lost was about 1%; above this temperature, the sample started to lose mass at a much higher rate of ca. 0.032 %/°C, and this tendency continued until the end of the experiment. The constant drop was the result of the progressive reduction of metal cations in the high-entropy structure and, therefore corresponds to the amount of evolved oxygen. Both the TG analysis and high-pressure hydrogenation indicate that the RS1 nanopowder underwent noticeable decomposition in a hydrogen atmosphere at 250°C. The RS1 sinter was not noticeably affected by high-pressure hydrogenation at 250°C, regardless of whether the atmosphere was pure hydrogen or a 5 vol% mixture of H_2 in Ar. A significant mass loss was not observed until the temperature had exceeded 400°C, at which point the cations in the high-entropy oxide started to gradually reduce to their metallic form.

The MS process parameters determined by optimizing the synthesis of the RS1 nanopowder were used to obtain new 5-, 6- and 7-component HEOs with rock salt structures containing Fe and/or Mn in addition to or instead of Zn. RS3, RS5, RS6 and RS7 samples were successfully obtained after 36 h of MS, as with the RS1 sample. However, for the RS2 and RS4 samples, it was necessary to perform the MS process for 72 h in order to obtain a single-phase material.

SUMMARY:

The optimization of mechanochemical synthesis allowed for direct synthesis of 7 different multicomponent compositions of nanocrystalline HEOs. The high-entropy rock salt structure of the studied RS1 nanopowder was incapable of absorbing hydrogen and not fully stable when exposed to a reducing hydrogen atmosphere. However, 5 h of thermally treating the nanopowder in air at 1000°C stabilized the cations in the rock salt structure. The results of PCT and XRD investigations clearly show that pure hydrogen at temperatures of up to 250°C and a pressure of up to 40 bar does not significantly impact the structure of the RS1 sinter. In addition, thermogravimetric analyses in a 5 vol% mixture of hydrogen in argon proved that the sinter retains full chemical stability up to 250°C , which leads to the conclusion that HEO sinters exhibits significantly higher chemical stability than their nanopowder forms.