In situ study of thermal reduction of CuIrOsRuRh, AgIrOsRuRh, AuIrOsRuRh high entropy alloy solid solutions (A31-1 152)

Proposer: Matthias Arenz
Co-Proposer: Kirsten M. Ø. Jensen, Rebecca Pittkowski
Beamline: SNBLII -BM31 / **Shifts**: 9
Dates: 03 Jun 2022 - 07 Jun 2022
Local contact: Dragos Stoian

1. Abstract

High entropy alloy (HEAs) nanoparticles have in recent years received immense interest, as their potential in catalysis has been uncovered. In the experiment, we investigated HEA synthesis via thermal decomposition from a single source precursor. We combined in situ XRD and XAS to study the formation of high entropy alloy materials based on six metals. The aim was to elucidate the formation mechanism by combining insight into the reduction mechanism of individual precursor elements and the crystallization behavior of the solid-solution precursor, to elucidate what determines the formation of single-phase mixed particles and which factors lead to phase separation.

2. Experimental Details

The experiments were performed in a capillary reactor available at the beamline. The precursors prepared in our home lab were transferred into 0.8 mm quartz capillaries and were secured in place with quartz wool. The samples were heated with a hot-air jet blower available at the beamline while X-ray diffraction and X-ray absorption spectra were collected consecutively. The samples were heated in a reductive gas flow of H_2/He to a temperature of 500 ℃. For comparison, X-ray absorption spectra were also collected of the individual metal precursors which are used to prepare the solid solution precursors, as well as of metal foils of the individual elements and metal salt precursors.

3. Results

The formation mechanisms of the Cu-containing high entropy alloy material, which shows the most complex formation mechanism of the samples analyzed during the experiment, is shown in *Figure 1*. In the contour plot of the diffraction patterns (*Fig. 1a*), the formation of two crystalline intermediate phases is found, alongside the metallic hcp alloy phase that gradually forms. The different regimes in the reduction process are indicated by the dashed lines in the contour plot. The first intermediate crystalline phase that appears is present in a temperature range from 130 to 200 ℃ (Bragg peaks at 7 and 10 ° 2 theta), and the second phase that forms consecutively is then appearing at 200 ℃ and is present up to temperatures of 400 ℃. The initial very crystalline phase can be attributed to the crystallization of Cu(I)Cl, and the phase forming consecutively can be attributed to a crystalline copper phase (*Fig. 1b*). Analysis of the XAS data confirms such an intermediate reduction to Cu(I) and finally to Cu(0). No changes in the copper XANES edge after the crystallization of copper are observed. While no crystalline copper is found at temperatures above 400 °C, the XANES data still confirm the presence of copper in the sample (*Fig. 1c*). This was further confirmed by EDX analysis of the prepared sample. A slight shift in the Bragg peak

positions of the crystallizing hcp alloy phase could be attributed to the incorporation of copper, this is, however, not conclusive yet. We have also observed a similar shift to larger diffraction angles, which indicates a shrinking of the lattice parameter, for hcp phase alloys without the incorporation of copper.

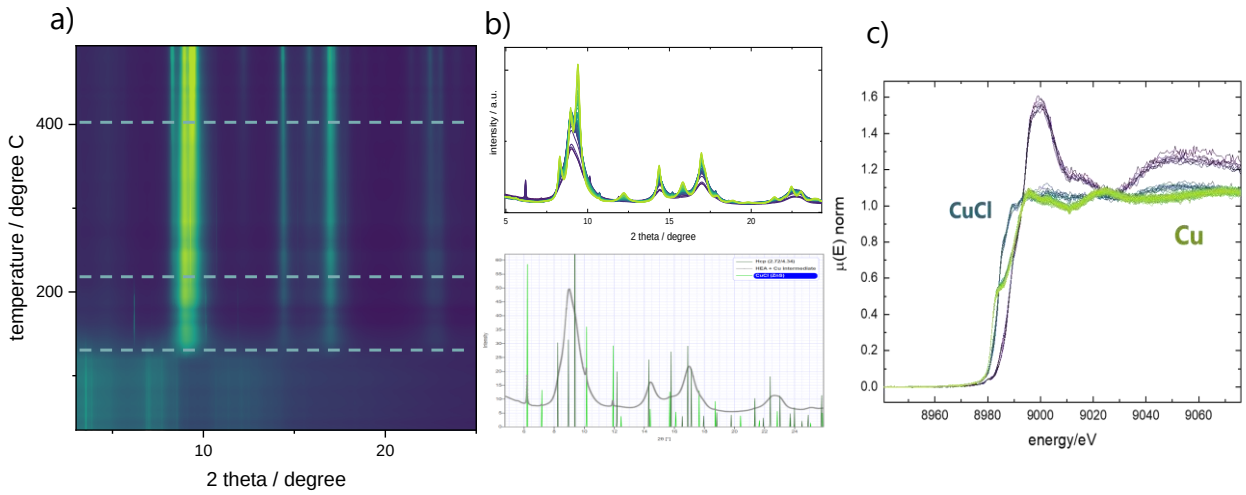

Figure 1a) Contour plot of Cu-containing hcp HEA materials of the diffraction patterns collected as a function of time during the reductive heat treatment b) diffraction patterns and references showing the crystalline copper intermediate phases forming and c) selected XANES spectra from the Cu K-edge showing the components found in the reduction process of Cu present in the sample.

4. Conclusions and future work

The experiments at B31 have shown that the formation mechanism of high entropy alloys are becoming more complex if elements of very different chemical properties are incorporated. We have for the first time observed the formation of several crystalline intermediates, which nature we were able to clearly identify by the combined diffraction and absorption data. The analysis is now extended by consecutive Rietveld refinement of the data, to quantify the lattice contraction of the hcp HEA as a function of temperature. To identify the nature of copper in the finally obtained material and confirm whether it is incorporated into the hcp HEA phase or is present as an amorphous copper phase, our collaborators at Aarhus University are performing HR-STEM/EDX mapping. We are further measuring total scattering data combined with PDF analysis of the formed HEA materials at an upcoming beamtime at P02.1/ PETRAIII.

5. Publications resulting from the work

We expect to publish the results once the data analysis is finished and we have obtained the HR-STEM/EDX mapping results from our collaborators.