ESRF Experimental Report

CH 5972: In situ study of the thermal reduction of high entropy alloy solid solutions

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1. Abstract

High entropy alloys (HEAs) have in recent years received immense interest as their potential in catalysis has been uncovered. In the work we investigated HEA synthesis via the thermal decomposition from a single source precursor. We compared in combined *in situ* XRD and XAS the formation of bimetallic samples to multimetallic samples to elucidate the formation mechanism and investigate the prerequisite factors for obtaining a single phase in the diffraction pattern.

2. Experiment details

Solid solutions of RuRhOsIrPt, IrRu, IrRh, IrPt, IrOs, PtRu, PtRh, OsRu, and OsRh single source precursor were prepared at University of Bern and taken to the ESRF. At ESRF the powders were filled into capillaries fitting to a reactor that allowed the streaming of a Ar/H_2 mixture while the capillary was heated at a constant ramp. During the heating ramp XRD and XANES measurements at the different metal edges were performed. The XRD data reveal the structural formation from the solid solution of the RuRhOsIrPt precursor to the reduced RuRhOsIrPt HEA as a function of temperature. The XANES data allow to follow the individual reduction of the precursor elements as function of temperature.

3. Results

The multimetallic and most of the bimetallic samples could be measured. An example of the temperature dependent XRD data recorded during the beamtime is shown in Figure 1 comparing RhIr and RhPt. It is seen that while RhIr forms a single fcc phase, three fcc phases are formed for RhPt respectively. Around 200°C the structural transition from the precursor structure to the fcc structure(s) occurs.

The temperature dependent XAS data, see Figure 2, show that the reduction of Rh and Ir leading to one phase occurs at a similar temperature, whereas the reduction of Rh and Pt that leads to multiple phases occurs at two different temperatures. Interestingly, the multimetallic RuRhOsIrPt samples form a single phase, although the elements reduce at different temperatures, see Figure 3.

Sequential Rietveld refinement was performed to follow the material formation mechanism of the fcc alloy in more detail. The lattice contraction, as indicate by the shift in Bragg peaks, can be followed in a plot of lattice parameter *a* as a function of temperature. Different slopes in the lattice shrinking are observed, which can be correlated with the reduction process as determined by analysis of the XANES spectra, which follows the reduction of each individual element.

The current hypothesis is that in the multimetallic phases the “atom exchange” pathways are too short to allow for phase separation, i.e., although Pt reduces first no combination of Pt atoms is possible due to “a frozen” state. By contrast, in bimetallic samples the formation of separated phases can not be prevented in case the precursor reduce at different temperature as there are “always atoms in direct contact”.

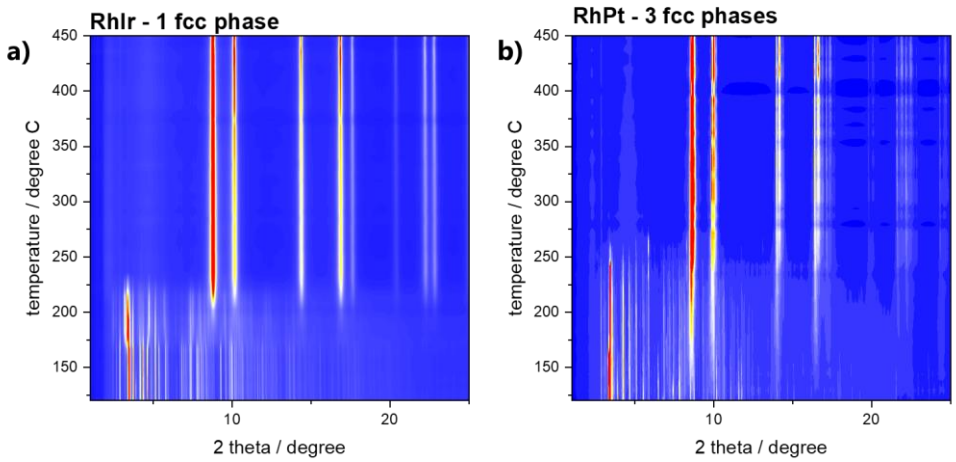

Figure 1. Overview of the temperature dependent XRD data recorded during the thermal reduction of the RhIr and RhPt solid solution precursors. The transition from precursor to fcc HEA at around 200 °C is clearly discernable. In case of RhIr single phase is formed while for RhPt three phases are discernible.

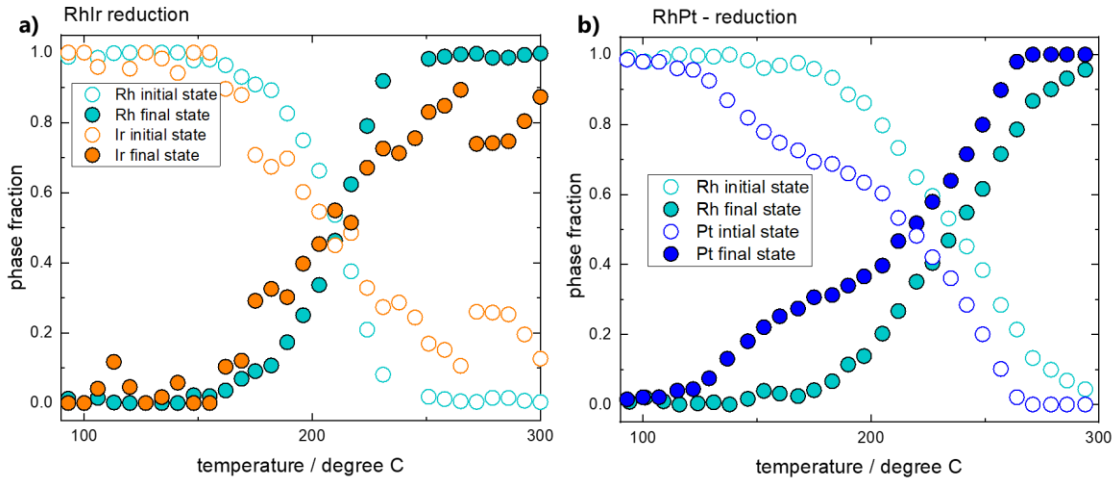

Figure 2. Analysis of the temperature dependent reduction of Rh and Ir (a) and Rh and Pt (b) extracted from the XANES data.

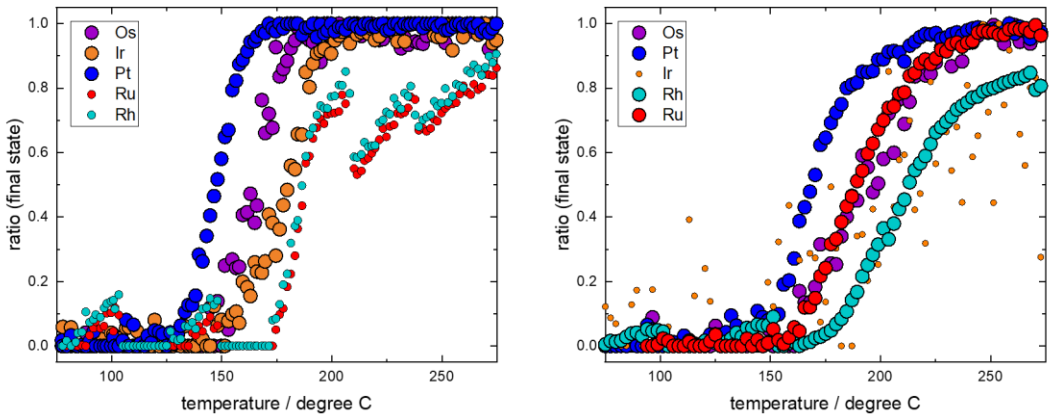

Figure 3. Analysis of the temperature dependent reduction of Os, Ir, Pt, Ru, Ru, in two HEA samples leading to a single phse. Rh and Ir (a) and Rh and Pt (b) extracted from the XANES data.

4. Conclusions and future work
The beamtime has been a success. Currently, we conduct further microscopic measurements on the samples.

5. Publications resulting from this work
Once the analysis is complete and we achieved a proper understanding, we are planning to publish the results in a joined paper with the ESRF staff.