

## 1. Abstract

High-entropy alloy (HEA) nanoparticles (NPs) have in recent years received increased interest due to their potential in catalysis. With the multi-dimensional compositional space provided by these materials, their catalytic properties can be tuned almost limitlessly. In this work, we investigated HEA synthesis via a recently developed solution-based synthesis using metal acetylacetonate salts as starting materials and oleylamine as solvent. By combining *in situ* XRD and XANES experiments, we were able to follow the formation of monometallic to multimetallic samples, and thereby uncover why only certain HEA compositions can be prepared, and why and when metal segregating takes place.

## 2. Experiment details

For each composition ranging from monometallic (Ag, Ir, Pd) to multimetallic NPs (AgIrPd, AgIrPdPt, IrPdPtRhRu and AgIrPdPtRu), precursor solutions were prepared by mixing the metal acetylacetonate salts with oleylamine under stirring at 50 °C in the beamline lab at ESRF. The precursor solutions were transferred to a capillary, which would be closed off by UV-glue and placed in the beam. The *in situ* XRD and XANES measurements were conducted using a simple, custom-made setup, previously used at beamlines at DESY and APS. The setup consists of an aluminum block, and heating is provided through two cartridge heaters, which was further connected to a thermocontroller provided by the beamline. Each *in situ* measurements was performed for approx. 2 hours at 235°C. During the heating ramp XRD and XANES measurements at the different metal edges were performed. The XRD data reveal the structural formation from the precursor solution to the reduced HEAs as a function of temperature. The XANES data allow to follow the individual reduction of the precursor elements as function of temperature to provide insight into how the sequential metal reduction proceeds for different metal compositions.

## 3. Results

The multimetallic and monometallic samples could be measured. An example of the time-resolved XRD data recorded during the beamtime is shown in Figure 1 comparing selected XRD datasets of (a) AgIrPdPtRu and (b) IrPdPtRhRu. It is observed that an initial fcc Ag phase is formed in the synthesis of AgIrPdPtRu, followed by the formation of a second Pd phase, which is accompanied by the formation of a mixed phase. Resultingly, three dominating fcc phases are formed by the end of the experiment. Likewise, a single fcc phase is formed initially in the synthesis of IrPdPtRhRu. However, a single fcc phase appear to remain throughout the experiment with a slight contraction of the unit cell as seen by the movement of diffraction peaks to lower Q values.

From the *in situ* XANES data in Figure 2, the reduction sequence can be compared. Here, it is observed for AgIrPdPtRu that Ag reduction appears already at the beginning of the experiment, followed by Pd reduction, while Ru and Pt appear to reduce around the same time in the reaction. Interestingly, Ir does not seem to reduce within the time of the experiment. In the absence of Ag in the reaction mixture, the same sequence appears to proceed. However, as evident by the XANES data, only Pd and Ru are observed to reduce. The lack of phase segregation might therefore either be related to the absence of the rapidly reducing Ag seed or since not all metal ion species are found to

reduce in the reaction. The current hypothesis is that the entropy that is normally introduced, when more elements are mixed, is not what drives the formation of multimetallic alloy structures. Nor is it the standard reduction potentials of the metal ion species, as the reduction sequence is found not to have any similarities to these intrinsic values. Instead, enthalpy might appear to be the main driving force to promote mixing at these more thermodynamic synthesis conditions.

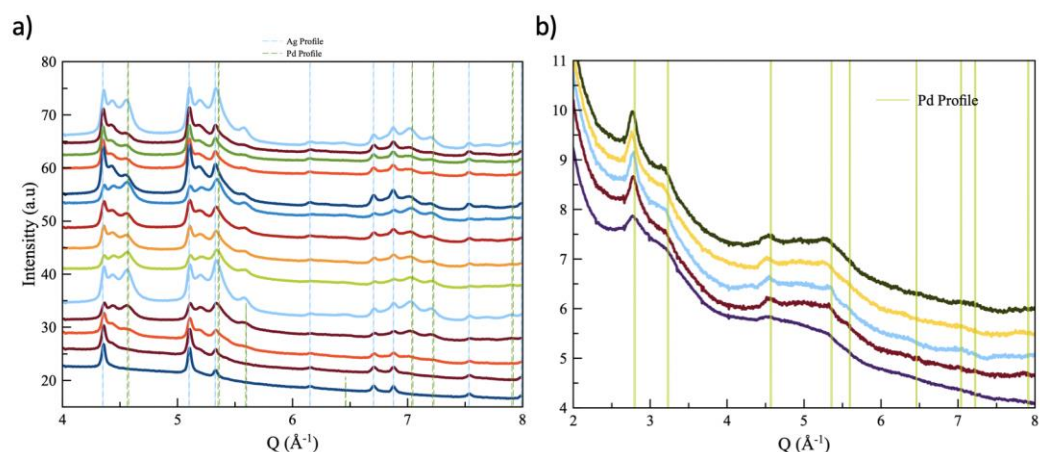


Figure 1. Overview of the selected in situ XRD dataset recorded during the synthesis of (a) AgIrPdPtRu and (b) IrPdPtRhRu NPs.

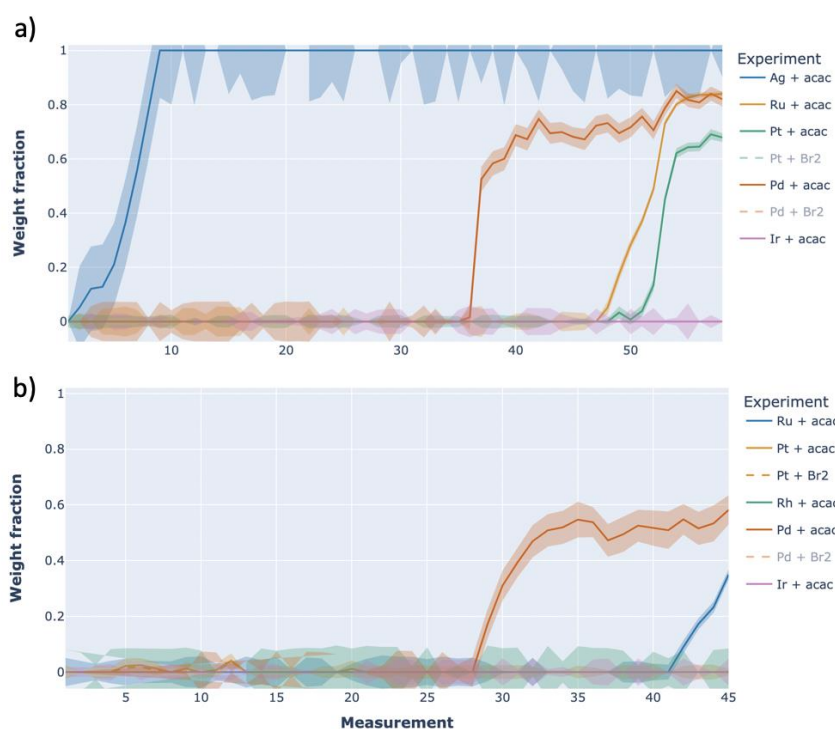


Figure 2. Analysis of the reduction of metal ion species in the formation of (a) AgIrPdPtRu and (b) IrPdPtRhRu NPs extracted from the XANES data.

#### 4. Conclusions and future work

The beamtime has been a success. We are currently analyzing the data, which will be combined with electron microscopic measurements as well as theoretical calculations to fully understand the nanoparticle structures and elemental mixing obtained.

#### **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.