ESRF Experimental Report

31-01 122: Understanding the unique role of Co inside the Pt-Co core-shell nanoparticles to boost the ORR activity

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Start of Experiment	04 Nov 2020	**Beamline/#shifts**	SNBL-BM31 / 15

1. Abstract

Due to the COVID restrictions the experiments could only be performed in remote mode by the Beamline staff Dr. Hermann Emerich and his team. Due to the lack of electrochemical experience of the Beamline Scientists and the complicated operation of electrochemical operando measurements it was decided with the Beamline Scientists to perform different experiments than the ones originally proposed. Thereby the beamtime could be used in a meaningful manner.
We decided to perform operando XRD/XANES measurements of the thermal reduction of solid solutions of so called single source precursors which lead to the formation of high entropy alloys (HEA)[1]. The BM31 beamline provided the reactor for the reduction reaction and heating system. As system we selected the system $Ru_{12}Rh_{29}Os_6Ir_{20}Pt_{32}$.

2. Experiment details

The solid solution of the $Ru_{12}Rh_{29}Os_6Ir_{20}Pt_{32}$ single source precursor was prepared at University of Bern and send to the ESRF. There the powder was 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 $Ru_{12}Rh_{29}Os_6Ir_{20}Pt_{32}$ precursor to the reduced $Ru_{12}Rh_{29}Os_6Ir_{20}Pt_{32}$ 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

An overview of the temperature dependent XRD data recorded during the beamtime is shown in Figure 1. It is seen that around 175°C a structural transition from the precursor structure to an fcc structure occurs. Rietfeld refinement of the XRD data reveals that during the transition the lattice parameter continuously changes from around 3.885 Å to ca. 3.850 Å, see Figure 2. For comparison the lattice parameters of Rh, Ir, and Pt are 3.803 Å , 3.840 Å, and 3.923 Å.[2] The change in lattice parameter is not linear and different temperature regions can be distinguished. In agreement with the temperature dependent XAS data, analyzed by Dragos Stoian from the ESRF, see Figure 3, the current hypothesis is that during the reduction process first the „Anionic“ Pt, Ir, Os precursor reduce. Possible intermediate complexes of lower oxidation state form through ion exchange. The reduction of the cationic precursor part (Ir, Ru, Rh) leads to the observed lattice contraction. After the complete precursor reduction a continuing lattice shrinking is observed that might be related to the annealing of defects, e.g. interstitial atoms, and/or diffusion of smaller atoms Ru, Rh to the bulk. Further experiments are required for a better understanding of the HEA formation mechanism. These have been performed in June 2021 and are currently analysed.

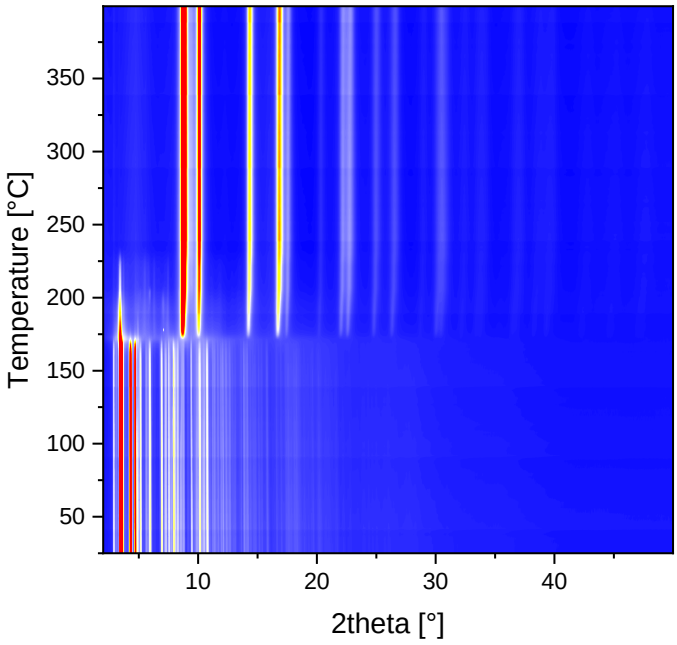

Figure 1. Overview of the temperature dependent XRD data recorded during the thermal reduction of the $Ru_{12}Rh_{29}Os_6Ir_{20}Pt_{32}$ solid solution precursor. The transition from precursor to fcc HEA at around 175 °C is clearly discernable.

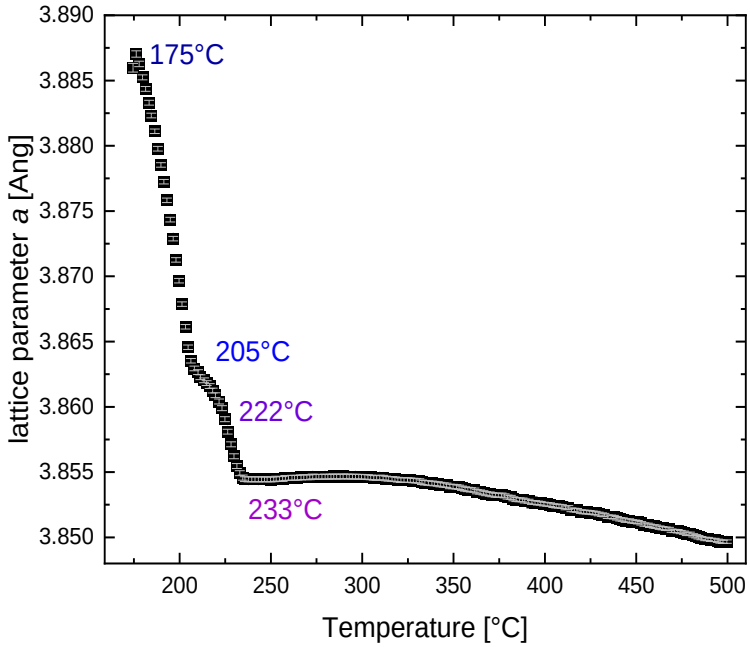

Figure 2. Temperature dependent lattice contraction as result of a Rietveld refinement of the XRD data.

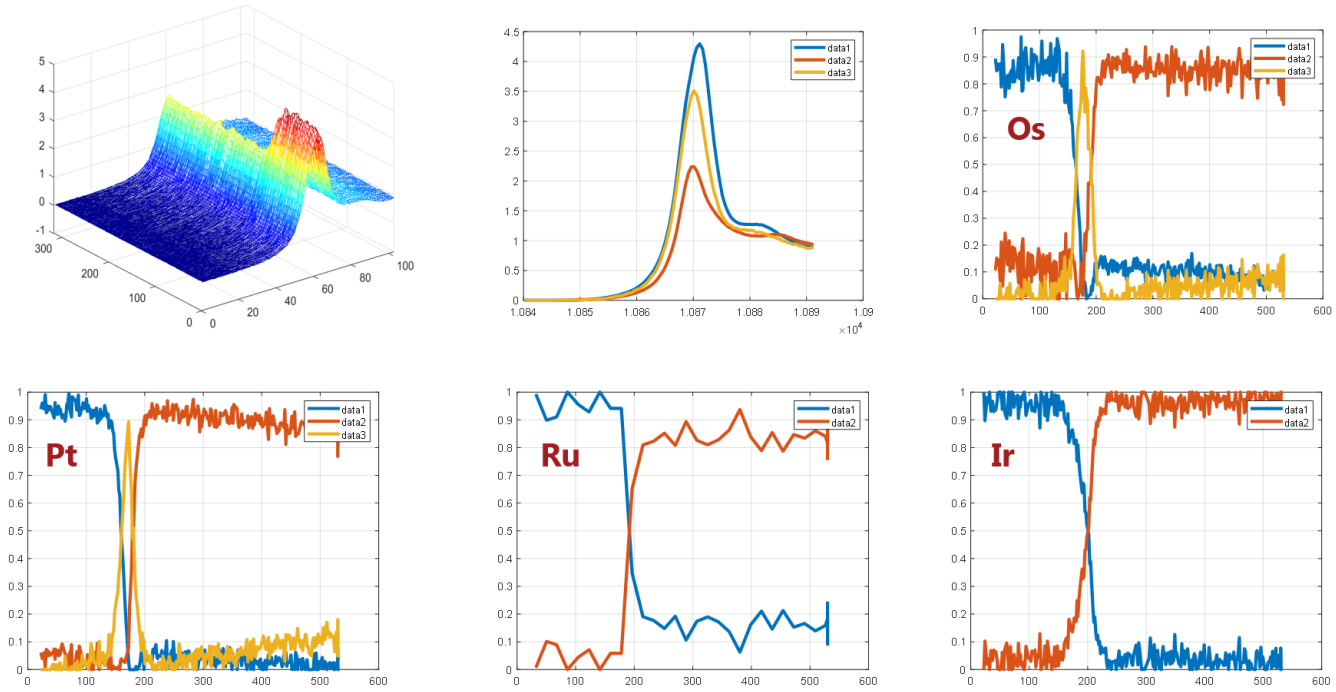

Figure 3. Preliminary analysis of the temperature dependent XANES data at the different metal edges.

4. Conclusions and future work

Under the challenging circumstances we judge the beamtime as success. Initial studies of the complex formation of HEA alloys from single source precursor solid solutions could be performed in a remote mode. Nevertheless, additional measurements are required for a better understanding. A data set recorded in June 2021 is currently analyzed.

5. References

1. Yusenko, K. V. *et al.* First hexagonal close packed high-entropy alloy with outstanding stability under extreme conditions and electrocatalytic activity for methanol oxidation. *Scr. Mater.* (2017) doi:10.1016/j.scriptamat.2017.05.022.
2. Wyckoff, R. W. G. *Crystal structures Vol.1*. (Interscience Publishers, 1963).

6. 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 that recorded and partially analyzed the data (XANES analysis).