In-situ TEM heating of bimetallic Fe/Au nanoparticles

Jenko, D.[1,2], Liebscher, C.[3], Majeric, P.[4], Rudolf, R.[4,5], Godec, M.[1], Friedrich, B.[6] and Dehm, G.[7]

[1] Institute of Metals and Technology, Slovenia, [2] Max-Planck-Institute für Eisenforschung GmbH, Düsseldorf, Germany, Slovenia, [3] Max-Planck-Institut für Eisenforschung GmbH, Germany, [4] Faculty of Mechanical Engineering, University of Maribor, Slovenia, [5] Zlatarna Celje d.d., Slovenia, [6] IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Germany, [7] Max-Planck-Institute für Eisenforschung GmbH, Germany

Magnetic Fe oxide nanoparticles (NPs) with modified surface chemistry are interesting material for potential biomedical applications. However, because of their high surface area, they react strongly with oxygen in air and oxidize. One solution to overcome this limitation is to coat Fe oxide NPs with other materials, such as Au, which is oxidation resistant and in addition also provides biocompatibility. Recently, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) have received a lot of attention and mainly Fe/Au core-shell nanostructures have been studied. These NP systems are very attractive for biomedical applications and as magnetic nanomaterial. The Au shell around the Fe core is enhancing the chemical stability of the NPs by protecting the core from oxidation and provides good biocompatibility.

One of the major problems with the application of nano-catalysts is their inherent instability and tendency to sinter and deactivate. The stability of promising new catalysts needs lengthy testing under reaction conditions before being developed further and implemented in industry, and to speed up this process, a greater understanding of the sintering process is needed. Generally, there are two main mechanisms that give rise to cluster and particle growth - migration and subsequent collision and coalescence of the particles, and Ostwald ripening, in which one particle will grow at the expense of another through inter-cluster transport. In this work different precursor combinations of Fe and Au containing salts were used in preparing the precursor solutions synthesized by Ultrasonic Spray Pyrolysis (USP) to obtain bimetallic Au/Fe NPs.

The behavior of bimetallic Fe/Au nanoparticles was studied at elevated temperatures during in-situ heating in a Transmission Electron Microscope (TEM). Microstructural characterization of the nanoparticles, such as differences in morphology (size and shape), chemical composition and their stability at elevated temperatures, was performed using conventional TEM (CTEM), high-resolution TEM (HR TEM) and Energy-Dispersive X-ray Spectroscopy (EDS) in a JEM-2200FS (JEOL, Japan), operated at 200 kV, and a probe-corrected Titan Themis 60-300 (FEI, USA) at 300 kV acceleration voltage. Samples for in-situ heating experiments were drop cast on an MEMS-based heating holder (DENSsolutions, The Netherlands). Different heating and cooling rates were used with a maximum annealing temperature of 1100 °C. It is found that Au NPs with an average size of 7 nm to 70 nm are decorating the surface of Fe-based nanoparticles, with an average size between 20 nm and 500 nm. The in-situ heating experiments established that the Au NP became mobile only above temperatures of >750C for prolonged annealing times of >1 h. For extended annealing experiments, the migration and coalescence of Au NPs was observed, whereas the Fe NPs remain mainly unaffected until the critical annealing time. After a critical annealing time, the growth of the Au particles proceeds until the whole NP agglomerate is disintegrating. The mechanisms involved in surface particle migration and coalescence will be discussed in the presentation, and also the possibility of Fe-Au alloy formation. An example of bimetallic Fe/Au NPs at room temperature and after in-situ heating at 1000 °C is shown in Figure 1.

Acknowledgements:

The authors acknowledge the financial support from the Slovenian Research Agency (research core fundings No. P2-0132 and P2-120) and bilateral project Slovenia/Germany BI-DE/17-19-12 (2017-2019).

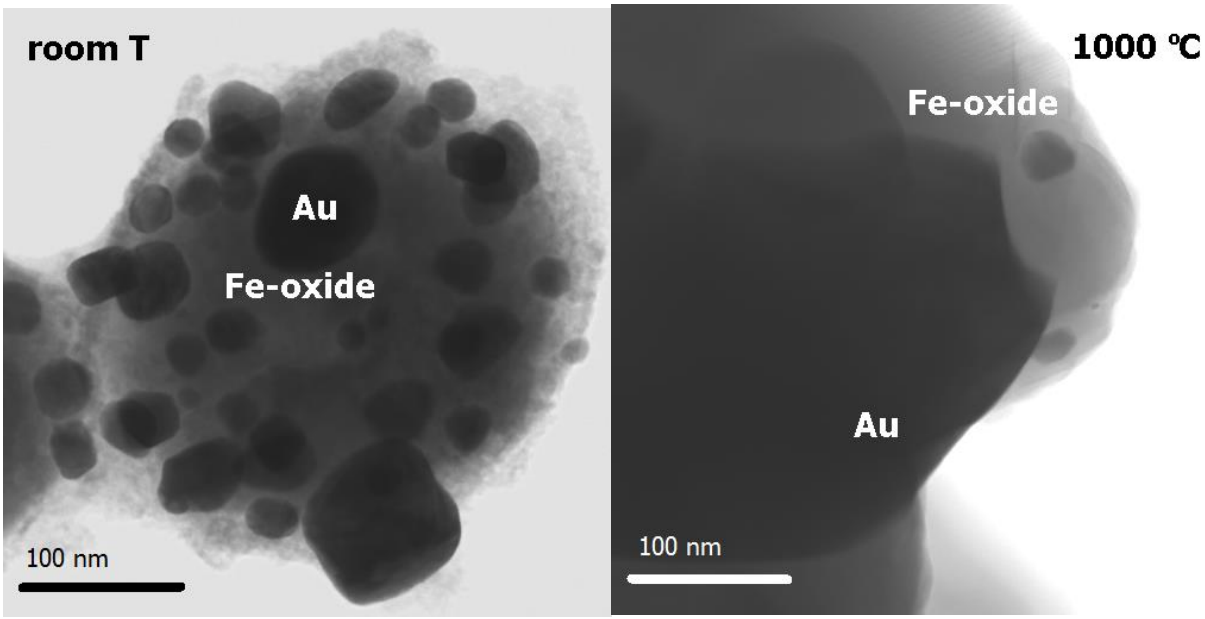

Figure 1: Scanning TEM (STEM) images of bimetallic Fe/Au NPs at room temperature and after in-situ heating at 1000 °C.