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Time-resolved Analytical Electron Microscopy with Single Nanosecond Electron Pulses

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In-situ TEM studies of chemical reactions or phase transitions at the nanoscale are often challenging due to the high speed of transformations, particularly at high temperatures. The temporal resolution of standard TEMs with continuous electron beams hardly exceeds the millisecond time scale. In the past two decades, ultrafast or dynamic TEMs (UTEM/DTEM), working with ultrashort electron pulses in pump-probe experiments, have revealed information at the nano- to femtosecond time scale [1, 2]. However, studies of irreversible transformations are still challenging because the commonly used stroboscopic approach is not applicable. The single-shot mode [2] is needed where one very intense electron pulse is used for imaging, electron diffraction, or electron energy-loss spectroscopy (EELS). Repulsion effects within the electron pulses, leading to the Boersch effect or space charge around the cathode, limit the spatial, temporal, and energy resolution. Here, we show how EELS can be integrated with single-shot studies, making analytical electron microscopy of irreversible chemical reactions with nanosecond time resolution possible.

In the setup in Strasbourg, a TEM with a disc-shaped photocathode and Wehnelt electrode is used that has been retrofitted with an additional condenser lens and mirrors for sending laser pulses onto the specimen and the cathode (JEOL 2100, modified by IDES) [3, 4]. In the single-shot mode, two nanosecond lasers are used to initiate phase transformations in the specimen and create photoelectron pulses. Proper tuning of the Wehnelt bias is necessary to optimize the intensity and energy width of the electron pulses. With single 7 ns electron pulses, a spatial resolution of 20 nm is obtained in imaging. In EELS, an energy resolution of a few eV is feasible in single-shot mode; however, a realistic core-loss spectrum needs rather intense electron pulses that significantly widen the energy resolution to 20-30 eV. Nevertheless, time-resolved quantitative analysis of the elements in the specimen is possible under these conditions [4, 5]. By varying the pump-probe delay, the transformations can be studied with a time resolution of a few nanoseconds.

As an application of analytical TEM with nanosecond resolution, we show a time-resolved study of an irreversible chemical reaction. The carbothermal reduction of nanocrystalline nickel oxide to elemental nickel was analyzed [5]. A layer of nanocrystalline NiO on an amorphous carbon film was transformed in-situ by a 7 ns IR laser pulse to elemental Ni. The IR pulse was focused onto a 150 µm spot so that many experiments were possible on one grid without changing the specimen. After an electronically adjustable delay, a 7 ns UV laser pulse was sent onto the photocathode to generate an electron pulse. The electron pulses were used for imaging, diffraction, and EELS. In imaging, the fast morphological transformation of the small NiO crystallites to larger Ni crystals was observed. In diffraction, the reaction was seen as the transition between the different crystallographic structures of NiO and Ni. EELS allowed the time-resolved quantitative analysis of the specimen. In this particular reaction,

imaging and EELS show that the reaction proceeds in the time interval 1 – 3 µs after the laser pulse. However, time-resolved diffraction showed that crystalline Ni only appears 30 µs after the pulse, proving that a short-lived transient phase of liquid Ni was present during and after the reaction. The analysis of the composition as a function of time showed that it is a reaction of first-order (Arrhenius-like), which, in turn, is understandable if the liquid Ni acts as a diffusion channel for carbon atoms.

Hence, dynamic TEM with nanosecond pulses is a versatile tool for analyzing fast irreversible processes with high temporal resolution. Furthermore, the integration of EELS provides the analytical information so that the composition of the specimen can be determined as a function of time with nanosecond resolution, and the kinetics of fast reactions can be studied at the nanoscale. In this presentation, additional examples for irreversible and reversible transformations [6] will be shown [7].

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