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PREPARATION AND TEM CHARACTERIZATION OF INTERFACES IN CO-SINTERED METAL-CERAMIC COMPOSITES

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MOTIVATION

Tape casting with subsequent co-sintering can be used for manufacturing metal-ceramic composites with a high efficiency for a wide range of products, e.g. fuel cell technology or surgical instruments. The mechanical, chemical, and long-term properties of the products are mainly determined by the interface of the components, which requires a complete understanding of its microstructure in the nanoscale. Thus the established characterization methods (optical and scanning electron microscopy) must be supplemented with imaging and analytical transmission electron microscopy (TEM). The key enabler for a successful TEM investigation is a sitespecific preparation method, which is very challenging for a combination of different classes of materials.
A well-established preparation method is Focused Ion Beam (FIB) technique. The in-situ lift-out technique allows to choose the region of interest with a submicrometer precision. Due to the porosity of a sintered material a stabilization by infiltration with an epoxy material and subsequent curing was necessary. The final TEM-sample covers several micrometers on both sites of the interface.

For the imaging characterization of complex materials the Scanning TEM technique (STEM) leads to the best results. This way of operation enables the combination of imaging of lattice defects and chemical information, e.g. from Energy-Dispersive X-ray spectroscopy (EDX) or Electron Energy Loss Spectroscopy (EELS). The EEL spectroscopy of the near-edge structure, especially of the oxygen edge enables to understand the chemical bindings of the involved elements. Structural information can be achieved by electron diffraction.
A major result are differences in the ceramic microstructure in the vicinity of the interface. The interface is decorated by precipitations of steel alloying elements. The density of precipitations in the steel decreases rapidly in a region close to the interface. The knowledge about the phase configuration at the phase boundary is a precondition for the understanding its corrosion behavior and the key to a long term stable design.

PREPARATION

In the previous two decades, the Focused Ion Beam Technique (FIB) has been well established as most efficient way for TEM target preparation. The utilization of micromanipulators in terms of the in-situ lift-out technique allows to choose the target region with sub-micron precision.
We used a Carl Zeiss NVision 40 SEM-FIB tool, equipped with a Kleindiek micro-manipulator system for the final steps of TEM target preparation. A materialographic intersection perpendicular to the phase boundary between the stainless steel 17-4PH and an Yttrium stabilized zirconium oxide (YSZ) was performed to detect the interface to be prepared. A subsequent FIB cutting visualizes the structure of the interface with an intermediate resolution in a much better quality than mechanical polishing (Figure 1). Pores in the ceramic material or at the interface may lead to strong curtaining effects during preparation. If this leads to a loss of mechanical, the so-called “refill-technique” is a suitable approach: FIB milling will be interrupted after identification of the target region, and the pores will be filled manually with a glue, e. g. M-Bond 610. After curing the glue, the preparation can be continued since the specimen now behaves like a compact material (Figure 2). The TEM-sample will be extracted and mounted to common grid.

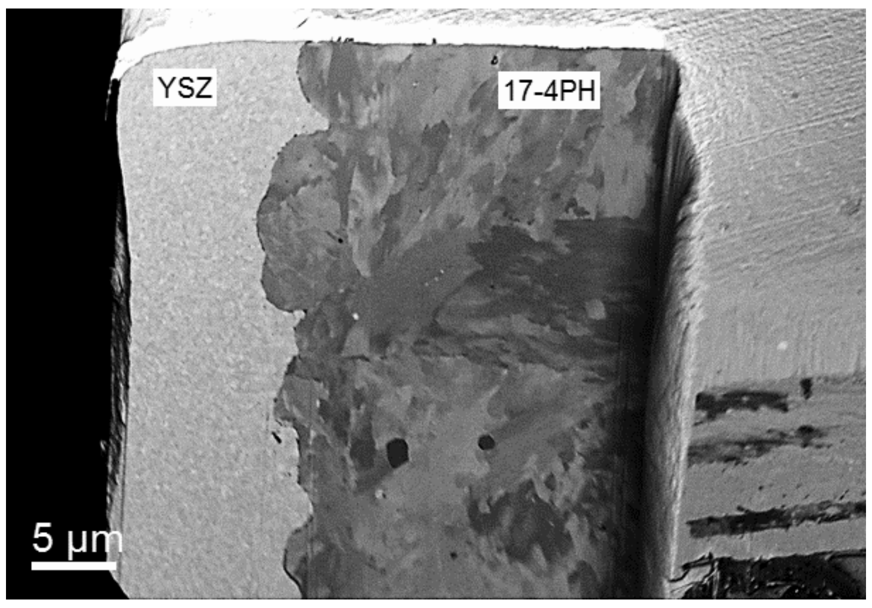

Figure 1: FIB cut close to the surface of 17-4PH stainless steel (right part) coated with YSZ (left edge). This interface between metal and ceramics is well visible and allows an optimum placement of the TEM lamella to be extracted.

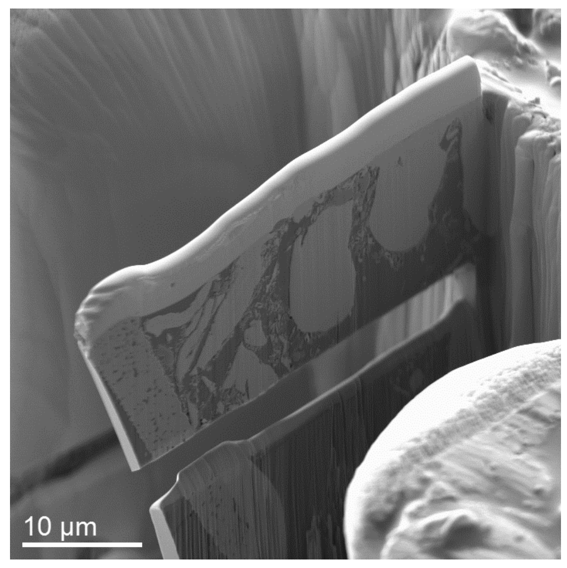

Figure 2: Sample filled by epoxy-based glue. The TEM lamella contains the steel part and the YSZ layer (left region, vertical).

(S)TEM IMAGING USING ADVANCED DIFFRACTION CONTRAST

A Carl Zeiss Libra 200 TEM tool was used, equipped with a monochromator, a CEOS probe corrector, an in-column energy filter, to be operated in EELS and EFTEM mode, a pre filter and a post filter HAADF detector, and an EDX analysis system. The combination of the post filter STEM-HAADF detector with a contrast aperture enables to adjust a diffraction contrast. This way of operation is less sensitive to small bending of the foil and the structural details can be recognized more clearly. Furthermore the STEM technique focusses a higher intensity on a small location, which enables to transmit a larger foil thickness.
Remarkable changes of the ceramic’s microstructure were observed up to a distance of about 1 to 2 µm from the interface (Figure 3). The grains near the interface are larger and a strong appearance of twinning is visible, which can be explained by the transition from the tetragonal to the monoclinic ZrO_2 phase. The phase transition occurs only in case of a sufficient binding between steel and YSZ only as to be seen in left part of figure 3. In case of delaminations like in the right part of the figure the original appearance of reaches until the phase boundary.
Depending on the sintering parameters, the precipitation behavior of the steel close to the surface is influenced. The fine dispersed precipitations with a diameter of about 10 nm in the steel, which are not present in a distance of about 100 nm from the interface (Figure 4).

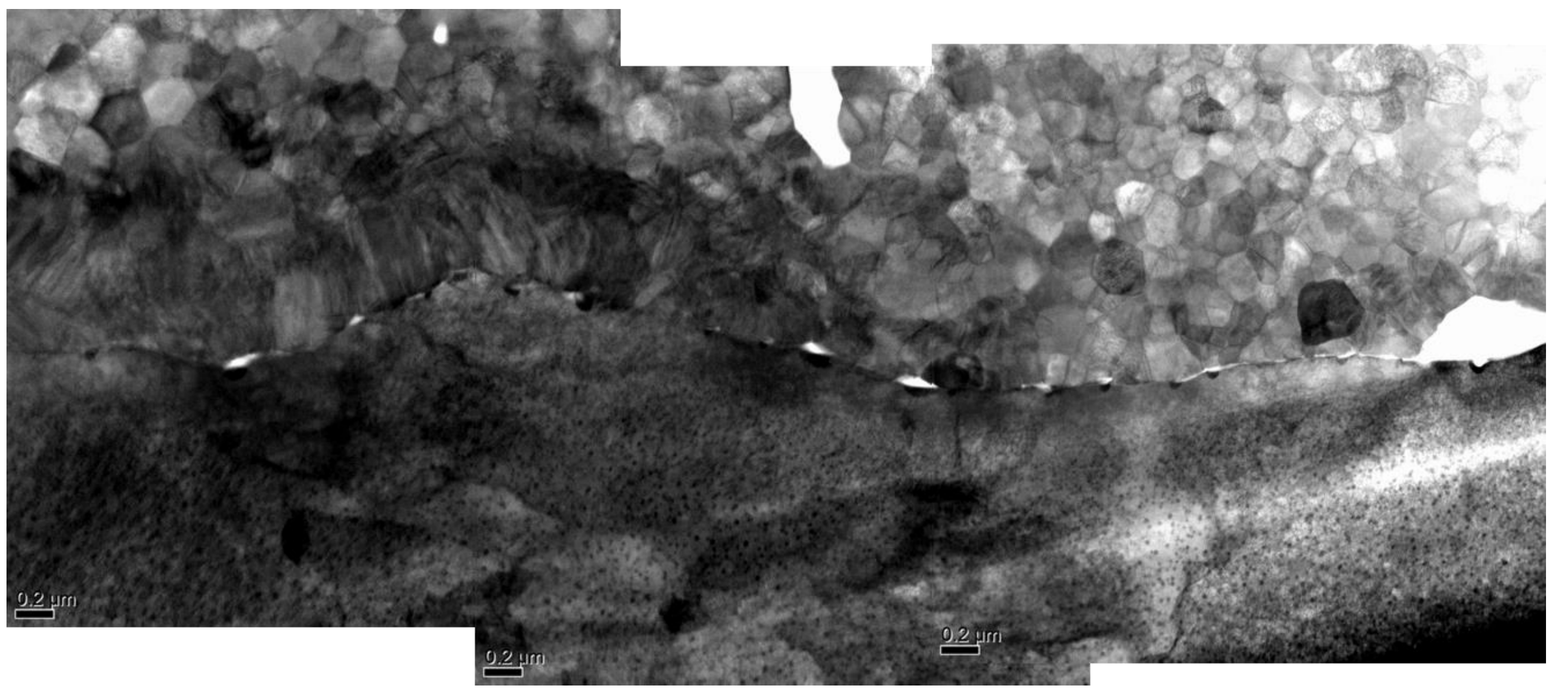
Figure 3: Phase boundary between ceramic (upper part) and stainless steel 17-4PH (lower part). Note the different grain morphology of the ceramic near the boundary at regions, where the good binding to the steel is given (left part).

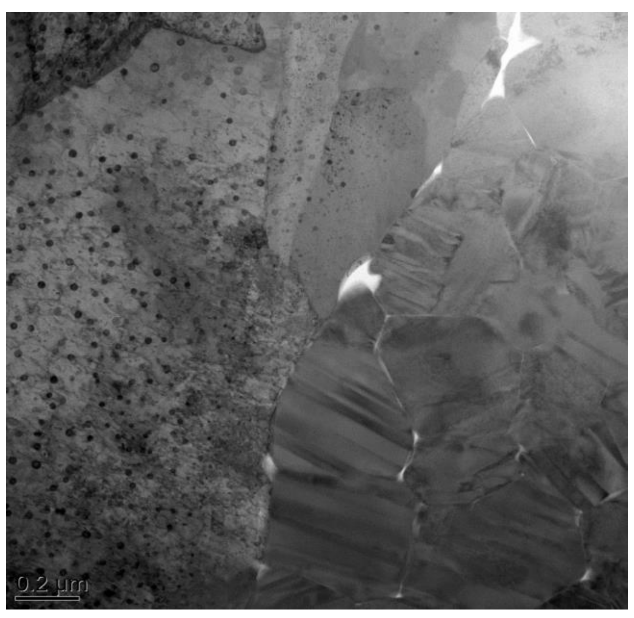
Figure 4: Phase boundary between steel (left) with precipitations (dark spots) and ceramic. Note the region free of precipitations near the phase boundary.

ELEMENTAL ANALYSIS

The EDX method in STEM mode was employed for a detailed analysis of the chemical composition of the sample near the interface. Spectrum imaging takes into account all elements existing in the materials. In Figure 5, a typical region with a grain boundary is imaged. The EDX mapping reveals that some alloying elements of stainless steel form precipitates at the interface with a size of a few 10 nm. There is a copper particle in the upper region of the phase boundary and 2 particles of chromium in the main region directly at the interface. The understanding of the precipitation processes at the interface seems to be the key for the corrosion behavior at the interface, which is currently one of the issues before bringing this technology to broad application.

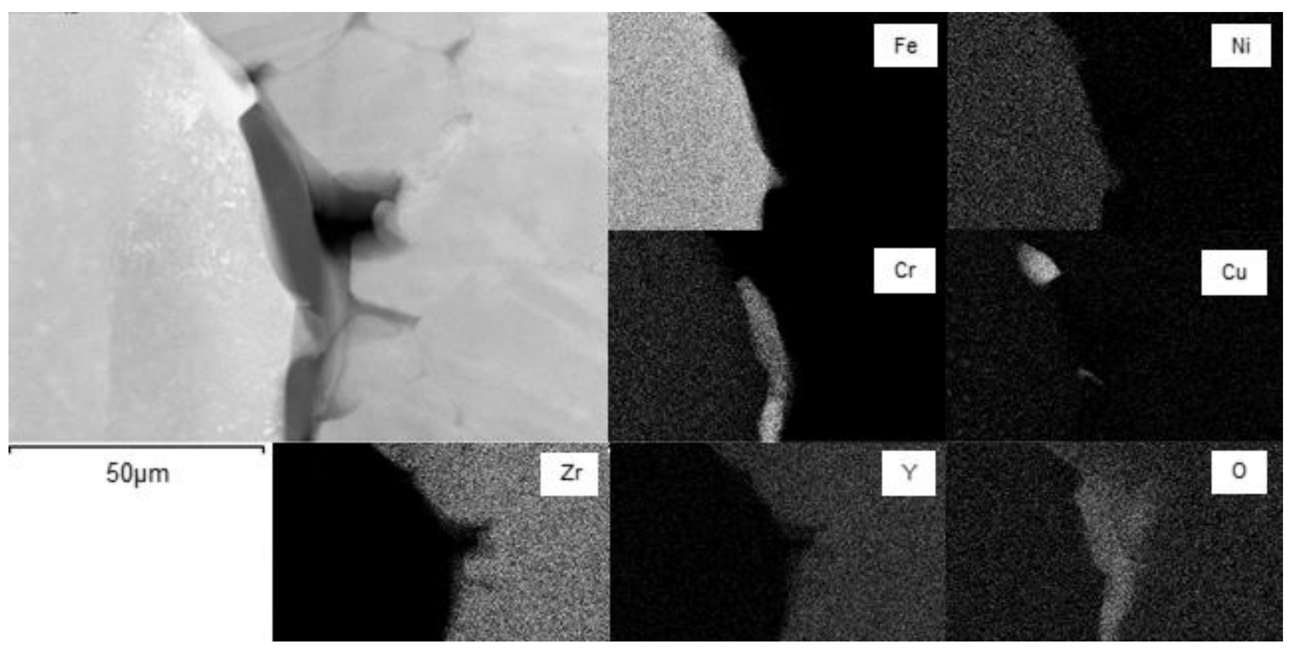

Figure 5: STEM dark field image of the interface between steel (left side) and ceramic (right part): upper left figure and elemental mappings using EDX in TEM of the same region (right and lower figures).

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