Target preparation and characterization of interfaces in co-sintered metal ceramic composites using imaging and analytical Transmission Electron Microscopy

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A new method for the production of metal-ceramics composites is co-sintering of a common produced green body. Detailed analysis of the interfaces is a precondition to understand the materials behavior and to align the process parameters for a reliable product. FIB-based target preparation enables a subsequent TEM observation. In addition to imaging preferred in STEM mode the elemental analysis using EDX and EELS leads to a comprehensive description of the interfaces.

Keywords: Ceramic, Composite, Interface, FIB preparation, Analytical TEM, STEM

1. Introduction

A new method for the production of metal-ceramic layered composites is co-sintering of both materials, combining powder-based ceramic technology and powder metallurgy to a common green body as well as a subsequent thermal treatment to the composite. This technology is currently under development and enables a strong step ahead in terms of efficiency, however, it requires still research for finding proper manufacturing parameters, which guarantee a reliable production. Possible applications are surgical instruments, where conductive and isolating parts have to be combined, advanced energy systems like fuel cells and filter elements [1].

Depending on the application and the requested properties of the final product as well as the specific use-case, porous or dense ceramic or metal parts are designed. A precondition for the functionality and the quality of the product is a robust and reliable connection of the components, determined by the interfaces between the materials involved. Particularly, the binding between different classes of materials, metals and ceramics, and the interactions between these materials have to be studied on the nanoscale. Transmission Electron Microscopy (TEM) provides high local resolution required, for imaging and for analytical studies such as of elemental composition, chemical binding and structural investigations.

An important precondition for a successful TEM analysis on a given and complex material system is a reproducible preparation method. We employed the Focused Ion Beam (FIB) technique and particularly an in-situ lift-out preparation of an interface region.

Fig. 1 Cross section of a stainless steel 17-4PH, coated with an yttria-stabilized zirconia (YSZ) layer

The composites consist of zirconia grains stabilized with 3 mol% yttria (Yttria stabilized zirconia - YSZ) and of stainless steel 17-4PH (Fig. 1). This steel contains high amounts of chromium (15.3%), nickel (4.5%) and copper (3.25%), respectively. The interface reactions during the thermal processes have to be taken into account and controlled.
2. Preparation techniques

In the previous two decades, the Focused Ion Beam Technique (FIB) has been well established as most efficient way for TEM target preparation [2]. 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 micromanipulator system for the final steps of TEM target preparation.

Firstly, the target region was uncovered from surrounding material. In case of the real constructions the amount of this material around often exceeds the opportunities of FIB milling in a relevant timeframe. Here a materialographic intersection through the layer system was performed to detect the interface to be prepared [3]. A subsequent FIB cutting provides visualizes the structure of the interface with an intermediate resolution in a much better quality than mechanical polishing (Fig. 2).

During the realization of the lift-out procedure the different milling rates of the materials have to be taken into account, especially at the primary steps, where the target region has to be released. In case of larger dimensions of the ceramic part the electrical conduction to ground has to be ensured to avoid charging, e.g. by prior deposition of a metallic layer. The complete sequence of the lift-out procedure was reported in [4]. It should be noted that the utilization of different detectors enables an excellent Scanning Electron Microscopy SEM-imaging at the lamella (fig. 3) in terms of structural details and z-contrast, which allows to prepare high quality samples with optimum thickness and the requested homogeneity.

Pores in the ceramic 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” [5] is the technique of choice: 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 (Fig. 4).
3. TEM methodology

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 an illumination angle of 15 mrad with a contrast aperture enables to adjust a diffraction contrast [6]. Contrarily to the common contrast in TEM mode using parallel illumination, this mode integrates over a range of incoming directions, consequently a range of deviation parameters. Thus, the imaging is not so sensitive against small deviations from the exact Bragg condition, e. g. by lamella bending, and leads to a more homogeneous contrast across large areas. In STEM mode, the whole intensity is focused to a spot, and therefore, a relatively thick lamellae can be transmitted [7], which is beneficial for elemental mappings with intermediate local resolution based on the EDX signal.

EDX analysis in the TEM is a very powerful tool for identification of phases on the nanoscale due to the reduced exited region. For application of EDX-analysis some parameter variations compared to imaging are recommended. The contrast aperture has to be removed to avoid a strong copper signal, which would exceed the signal of the excited range.

An alternative is to operate the instrument in dark field mode or to employ the filter entrance aperture in combination with a camera length which fits to the diffraction disk diameter.

Chemical composition of samples with preferably low Z elements and information about chemical bindings can be determined using Electron Energy Loss Spectroscopy (EELS), however, for specimens with a lower thickness [8]. For this purpose it is recommended to go back to FIB-system and continue thinning the regions of interest to less than 70 nm. The materials we were working on are very stable against atmosphere and additional observations can be done also after longer periods of specimen storage on atmosphere.

4. Results and conclusions

4.1 Imaging and structures

STEM imaging enables a more detailed characterization of the interface between steel and YSZ, and also small pores (Fig. 5). It is possible to detect on the nanoscale if local delamination occurs directly at the interface or a few nanometers away in the material (Fig. 6). Small cracks in the vicinity of the interface seem to be caused by thermal stress caused by cooling down from the temperature of the sintering process.
Remarkable changes of the ceramic’s microstructure were observed up to a distance of about 1 - 2 µm from the interface (Fig. 7). The grains near the interface are larger and a strong appearance of twinning is visible. There are more voids at grain boundaries and grain boundary triple points in the near-interface region than far away, which can be explained by the transition from the tetragonal to the monoclinic ZrO₂ phase [9] which obviously occurs in case of a sufficient binding between steel and YSZ only (Fig. 8).

Depending on the sintering parameters, the precipitation behavior of the steel close to the surface is influenced. The fine dispersed precipitations are not visible in a distance of about 100 nm from the interface (Fig. 9). Large precipitation are visible at the interface, which were analyzed using EDX (see next chapter).
Fig. 7 Interface between YSZ (right) and steel (left). Note the different microstructure of the ceramics in a region of about 1 µm next to the interface.

Fig. 8 (lower image) Microstructure changes of T-YSZ (upper part) next to the interface to steel (lower part): Note that the microstructure changes only established at the left region where a good binding between both materials is given. On the right side we observed delamination starting from a void, and ceramic grains with a grain size as in the bulk material and without twins.

Fig. 9 Interface between steel (left side) and YSZ (right side): Note the precipitations in the steel, here as dark spots, with a size up to 10 nm, are missing at a distance of about 100 nm from the interface to the ceramics.
For porous sintered ceramics, a poor ordering of the individual grains near the metal/ceramic interface (Fig. 10) occurs. Whereas a fraction of the YSZ grains shows a well bonding to the steel, also pores in the range of several µm could be detected, which are potential starting points of delaminations. The elemental analysis, here single EDX spectra acquisition as described in the next chapter, allows an identification of the grains and precipitations near the interface.

Contrarily to the pure copper particles in case of dense sintered material, copper oxide particles (Fig. 10) were observed. This may be caused by the higher oxygen supply during the sintering due to the pores. We found that the binding between steel and ceramic grains is reasonable and not influenced by the porosity.

**Fig. 10** Interface between porous YSZ (left) and steel (right) with the identification of grains by EDX analysis: Note the disordering of the grains directly at the interface and large pores, and the appearance of a copper oxide precipitation. Small amounts of Cu detected in all materials are caused by the Cu grid, and has to be distinguished from real copper enrichments.

**Fig. 11** Interface between steel (left), upper left image and elemental mapping of the main elements of the steel (Fe, Ni, Cr, Cu) and YSZ (Zr, Y, O). Cr₂O₃ and Cu are detectable at the interface.
4.2 Elemental analysis

The EDX method in STEM mode was employed for a detailed analysis of the chemical composition of the sample near the interface. Using spectrum imaging [10] takes into account all elements existing in the materials. In Figure 11, a typical region with a grain boundary is imaged, finding a reasonable compromise between required pixel resolution and analysis time. 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 beside chromium rich particles directly at the interface. A comparison of single spectra in all components using higher count rates reveals an oxygen signal (O K ionization edge).

![Fig. 12](image12.png)

**Fig. 12** EEL spectra of the steel, YSZ and the Cr₂O₃ particle to confirm its oxidic nature due to the presence of oxygen.

![Fig. 13](image13.png)

**Fig. 13** Interface between YSZ (upper part) and steel (lower part), identification of a ceramic particle in the steel (marked). At the right side the particle in close up view and elemental mapping of this region, using high magnification.
Because of the superposition of the chromium L and the oxygen K lines in the EDX spectrum, EELS (energy resolution about 1 eV compared to about 130 eV for EDX) was applied to identify the Cr-rich region in the sample. The spectra in Figure 12 indicate the existence of Cr and O in this region. The features near the of oxygen K ionization edge are different for the Cr-containing sample region and for YSZ, and are consistent to EELS O K edge features published for ZrO$_2$ [11] and Cr$_2$O$_3$ [12].

A special point of interest in case of co-sintered material is the near-interface region. For dense sintered materials, the interface was usually well defined. Nevertheless single ceramic particles were found in steel in the vicinity of the interface (Fig. 13). Elemental mapping using a high local resolution reveals a ZrO$_2$ particle surrounded by steel, which is not related to a grain boundary. The two smaller grains at the grain boundary of the particle are containing Cu, which is an alloying element of steel. So the phase boundary between the ZrO$_2$ particle and steel seems to act as nucleation site for copper.

5. Summary and Outlook

The preparation of TEM samples of layered metal-ceramics composites was demonstrated using FIB based in-situ lift-out techniques, partly by using a stabilization with glue. For a detailed characterization of the material and the interfaces brightfield STEM was recognized as most efficient imaging technique. This technique allows additional EDX and EELS analysis for element analysis in a very convenient matter.

The analytical techniques are a precondition for the structural understanding of solid state physical and chemical phenomena at the interfaces for example in studies of the corrosion behavior.

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