Chapter 16

X-Ray Computer Tomography for Three-Dimensional Characterization of Deformation and Damage Processes

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Abstract The investigation of phase transformations in metastable ceramic systems such as zirconia often requires local phase analysis within the areas of interest. Electron backscatter diffraction is a suitable method. The effect of the combination with focused ion beam sample preparation was determined in this work. In addition metal matrix composite metal matrix composite honeycombs and foams as well as beads were investigated. The foams and honeycombs were composed of austenitic steel exhibiting Transformation Induced Plasticity (TRIP) and magnesia partially stabilized zirconia. Both components exhibit martensitic phase transformation during deformation, thus generating the potential for improved mechanical properties such as strength, ductility, and energy absorption capability. The aim of these investigations was to show that stress-assisted phase transformations within the ceramic reinforcement correspond to strong local deformation, and to determine whether they can trigger martensitic phase transformations in the steel matrix. To this end, in situ interrupted compression experiments were performed in an X-ray Computed Tomography Device (XCT). By using a recently developed reconstruction algorithm, local deformation was calculated and regions of interest were defined. Corresponding cross sections were prepared and used to analyze the local phase composition by electron backscatter diffraction. The results show a strong correlation between local deformation and phase transformation.

16.1 Introduction

Metal matrix composites (MMCs) have been in the focus of research and development for many years. The growing demand on light-weight materials with acceptable mechanical properties is one reason. In general, the metal matrix consists of low-density materials like aluminum or magnesium. A new generation of MMCs, the

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so-called TRIP-matrix composites, has been developed within the last decade [1, 2]. Its constituents are TRIP steel and Mg-PSZ ceramic particles. The steel matrix of these MMCs exhibits a TRIP effect (TRansformation Induced Plasticity), thus possessing excellent mechanical properties with concurrent high strength and high ductility [3]. The TRIP effect is caused by a deformation induced martensitic phase transformation from austenite (fcc) to α' -martensite (bcc) via an intermediate state of highly faulted austenite or ε -martensite (hcp).

There are three different Zirconia modifications; namely cubic ($2650 \text{ K} < T < T_m$), tetragonal ($1478 \text{ K} < T < 2650 \text{ K}$), and monoclinic ($T < 1478 \text{ K}$) [4]. The phase transformation from the tetragonal phase to the monoclinic phase is accompanied by a volume expansion of 3–5%, which leads to deformations in the areas surrounding the zirconia particles and high shear. The tetragonal high-temperature phase can be stabilized down to room temperature by the addition of certain stabilizers as Y_2O_3 , CaO, or MgO. Partially stabilized zirconia exhibits a stress-assisted martensitic phase transformation [5]. In the TRIP matrix composites, MgO partially stabilized zirconia (Mg-PSZ) is used. The combination of the deformation-induced phase transformation of the steel matrix with the stress-assisted martensitic phase transformation of the Mg-PSZ produces composite materials with high damage tolerance [6]. This opens up a wide field of application for high-strength materials that possess the capability of absorbing mechanical energy during, for example, crash loading.

Suitable designs for this purpose are in particular honeycomb structures, foams and hollow spheres. They offer a combination of low density and high energy absorption capability. Therefore, in situ deformation experiments of such specimens were performed by X-ray computed tomography XCT. The aim was, in addition to the three-dimensional mapping of deformation and damage, to investigate the relationship between local deformation and local phase composition. This should also allow statements on the trigger stress. Wide space occupied the development of the required investigation methods. For the in situ compression deformation in the XCT a special apparatus was developed and built. This allows forces up to 100 kN. Furthermore, it was necessary to carry out local phase analysis with a resolution of less than $1 \mu\text{m}$. A suitable method for this is electron backscatter diffraction (EBSD) [7]. This is a surface-sensitive method. The information depth is a maximum of 100 nm. In this near-surface area, no disturbances of the original deformation-related microstructure due to sample processing must be present. Therefore, methods of target preparation had to be developed. It was ascertained that the local chemical composition of the examined MMC has a decisive influence on the local phase composition. In particular, the ZrO_2 particles can be destabilized in the sintering process. This reduces the fraction of metastable (transformable) phases. The result is the formation of silicates and spinels from reactions of impurities in the powder constituents used and an associated diffusion of the stabilizers to the steel/ceramic interfaces. The consequence is a wide dispersion of the local phase composition. The corresponding distribution functions must be determined in order to be able to describe the influence of a deformation on the phase composition [8, 9].

Within this work the target preparation for a optimal EBSD and XCT analysis of composites was investigated [10]. One method for determining the mechanical

properties of small samples at relatively small forces is the small punch test. First researches has been conducted. Furthermore MMC foams [11] and honeycombs [12] were examined. The aim of these investigations was to show that stress-assisted phase transformations within the ceramic reinforcement correspond to strong local deformation, and to determine whether they can trigger martensitic phase transformations in the steel matrix. Besides, in situ interrupted compression experiments were performed in an X-ray computed tomography device. Furthermore composite beads with graded layer structures (prepared with the alginate gelation technology) were examined and valued with X-ray computed tomography [13].

16.2 Experimental Details

Figure 16.1 shows the used XCT CT-Alpha from ProCon X-Ray Garbsen. It displays the punctiform X-ray source, the rotation table and the flat detector. Alternatively, two different X-ray sources can be used. Three different detectors were used. The technical data are:

- Directional ray tube 225 kV, Feinfocus Garbsen, Germany, 2008
- Transmission tube 160 kV, Feinfocus Garbsen, Germany, 2008
- Detector Hamamatsu C7942SK-05, Hamamatsu Photonics K.K. Hamamatsu City, Japan, 2008, 2400×2400 pixel, $50 \mu\text{m} \times 50 \mu\text{m}$ pixel size
- Detector Dexela 1512, 1944×1536 pixel, $75 \mu\text{m} \times 75 \mu\text{m}$ pixel size
- Detector PerkinElmer XRD 1620 AN CS, Perkin Elmer Optoelectronics, Fremont, Kanada, 2008, 2448×2448 pixel, $200 \mu\text{m} \times 200 \mu\text{m}$ pixel size.

Fig. 16.1 Laboratory XCT with the main components 1 X-ray tube (left). 2 Turning device with sample plate (center). 3 Flat detector (right)

The device for in situ compressive deformation was manufactured by the company Hegewald & Peschke (Nossen, Germany) after co-development. Figure 16.2 illustrates the basic structure. It displays a transmission system that transmits the torque of an electric motor to a spindle. This spindle moves a pressure plate. The sample is located between this lower and an upper pressure plate. The load cell is firmly connected to the gearbox housing via flanges and a CFC tube. During movement of the spindle the sample and the CFC tube are simultaneously under compression and tension respectively. A CT scan is possible, because the entire system can be mounted on the turntable of XCT. The absorption of X-radiation by the CFC tube is negligible. The CFC tube used for the experiments was supplied by the Institute for Construction and Composite Construction e.V. (TU Chemnitz, Germany).

One method for determining the mechanical properties of small samples at relatively small forces is the small punch test [15]. Cylindrical discs are deformed with the aid of spherical pressure stamp in the middle. The entire load within the specimen is rotationally symmetric with defined areas of compressive and tensile loading. Figure 16.3 shows the basic arrangement. Because of the rotational symmetry, the method is very well suited for in situ investigations in XCT at low forces. In order to

Fig. 16.2 Schematic representation of the structure of the in situ device for pressure deformation [14]

Fig. 16.3 Basic arrangement of the small punch test [15]

avoid a superposition of the absorbance contrasts of sample holder and sample, the entire sample holder shown in Fig. 16.3 consists of Si_3N_4 . This material is characterized by extremely low X-ray absorption and high fracture toughness at the same time. In the present study, an in situ deformation device Deben CT5000 was used (Deben UK Ltd, Bury St. Edmunds Suffolk, UK). This is designed for forces up to 5000 N and a higher resolution in the XCT is possible, due to the small dimensions. It was installed for this purpose in a XCT ZEISS Xradia510 type. In this combination a volume resolution (voxel size) of $0.7\text{ }\mu\text{m}$ was possible at a sample diameter of 4 mm. Figure 16.4 illustrates the arrangement with installed deformation device. Part of the microstructure analysis was investigated in a SEM XL30 from Philips equipped with a EDX/EBSD-System from Edax. FIB preparation and characterization of the microstructure were performed in a FEI Versa3D dual beam system. This microscope is equipped with a 30 kV Ga^+ ion source. An EDX- and EBSD analytical system Team from EDAX was used. Phase analysis was carried out for single points or for defined scans. The topographic information was obtained using the forward scatter detector (FSD), which was positioned below the EBSD screen. The preparation in the Versa3D microscope was performed by milling of cross sections at sharp edges of the samples. Thus, areas in the range of $50\text{ }\mu\text{m}^2$ could be investigated. In addition, embedded and polished samples were used in order to get defined initial surface conditions for the FIB preparation. The final preparation step for the embedded samples was vibration polishing in a Buehler VibroMet2. The polished samples were coated with PtPd20 layers in the range between 0.1 and 0.5 nm using a Cressington 208 HR Sputter Coater. Lattice parameters for the phase identification by EBSD were taken from an ICDD database [16]. These data were also the starting point for the XRD-whole-pattern fitting process.

Fig. 16.4 Deformation instrument Deben CT5000 in XCT Zeiss XRadia510, left: X-ray tube, middle: deformation device on the turntable, right: X-ray microscope

To characterize the graded beads, the X-ray computed tomography (X-ray CT) was conducted using a Zeiss Xradia 510 Versa X-ray microscope (XRM). This XRM is equipped with a 160 kV tungsten target X-ray source and scintillator detectors filmed from the back by a CCD camera (2048×2048 pixel) through a microscopy system. Therefore the total magnification results from the geometric magnification of the cone beam multiplied by the optical magnification of the microscope. The volume reconstruction was done using the Zeiss XRM reconstructor software. This software works with a filtered back projection algorithm and an additional beam hardening correction method. Detailed parameters used for tomography studies as well as for volume reconstruction are given by Oppelt et al. [13].

16.3 Results and Discussion

16.3.1 *Target Preparation and Effect of Focused Ion Beam Sample Preparation*

If specimen areas of interest can be optically detected with an accuracy of approximately 0.5 mm, a metallographic ground preparation is possible. For this purpose, the samples are cut with a diamond saw, embedded in epoxy resin, ground and polished to a particle size of 1 μm . The last step is followed by vibration polishing with a SiO_2 suspension MasterMet2 from Buehler. This was done by a polishing machine VibroMet2 from Buehler. To ensure sufficient electrical conductivity of the samples,

all polished surfaces were coated with about 0.2 nm Pt/Pd (Cressington 208 HR Sputter Coater). All corresponding parameters are the result of an optimization process [9].

Another method of target preparation is Focused Ion Beam (FIB). Here, the areas of interest can be selected directly in the SEM. After determining a suitable cut surface, this is exposed by means of FIB and polished. It has been found that ceramic materials not only show the radiation damage known from metals and semiconductors, but also phase transformations are possible [10].

In case of metastable Y-PSZ and Mg-PSZ, phase transformations or damage were observed independence of the parameters ion energy, ion current and incidence angle. Damage was the dominating effect for angles of 72° while phase transformations occurred during FIB-preparation with 30 kV, 30 nA and 5° incidence angle. The expected local temperature increase due to the ion bombardment (30 kV, 30 nA) is about 700 K for ZrO_2 . Thus, the observed phase transformations could be explained on the basis of the increased temperature (700°C) in the corresponding Y-PSZ phase diagram. In case of Mg-PSZ, the transition temperature is 1083°C . The local temperature rise was obviously lower. The excitation energy for the observed phase transformation was smaller than expected from the phase diagrams of the thermodynamic equilibrium. Using 5 kV, 4.8 nA and 5° incidence angle no phase transformations and no damage were observed. Thus, these conditions are suited for the FIB preparation of metastable zirconia. The investigation of phase transformations in zirconia requires a separation between zirconia and the other phases of the structure. Otherwise cubic structures of the steel matrix, zirconia and precipitations cannot be distinguished. This discrimination was realized using the combination of EDX- and EBSD-mapping. One has to keep in mind, that the interaction volumes of EDX and EBSD are different. However the given zirconia particle sizes enable the definition of phase boundaries by EDX with a sufficient resolution. A complete analysis of a scanned sample contains the following steps [8, 9]:

- (1) Scanning of at minimum 10 typical areas for each sample:
For each point of a scanned sample area the EDX spectrum and the EBSP are analyzed simultaneously. The typical map size was $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ with a step size of $0.2\text{ }\mu\text{m}$.
- (2) Analysis of the EDX maps and determination of the threshold values at phase boundaries.
- (3) Filtering of the EBSD maps:
This is carried out on the base of the EDX threshold values and separation into different phase areas.
- (4) Calculation of the phase distributions within the different phase areas:
The decision for one of the possible phases for each EBSP is based on the number of detected diffraction bands on the one hand and the difference between the measured angles between the diffraction bands and the corresponding angles between expected lattice planes on the other hand (fit). The phase with the highest number of corresponding diffraction bands and the lowest fit is taken.

The aim of the analysis of the target preparation was to study the influence of a FIB preparation on the phase composition of Mg-PSZ and Y-PSZ. Figure 16.5 illustrates a typical FIB cross section preparation.

As a first step, a platinum layer is deposited on the sample surface in order to get a defined cross section with little curtaining and without further damage of the sample. A metal-organic compound is used as a precursor for Pt. Typically this is dissociated with the aid of the ion beam and the metal is deposited. During the first seconds of this process, interactions between the ion beam and the sample surface have to be considered. Modifications may be necessary in case of fine sensitive surface structures. The stopping range of ions is in the same order of magnitude as the depth of possible damage. Therefore electrons may be used for the formation of a first layer of Pt. After deposition of the first layer of Pt atoms the damage stops. The second step is milling at an angle perpendicular to the sample surface followed by low energy polishing as a third step. As a result the sample surface is characterized by a damage depth Y smaller than the EBSD information depth $[10]$.

Figure 16.6 shows a typical fractured surface of Y-PSZ. As it can be clearly observed, the structure was bimodal with grains in the range of $10\ \mu\text{m}$ and below

Fig. 16.5 Scheme of the sample damage during FIB cross sectioning $[10]$

Fig. 16.6 EBSD phase analysis on a fractured surface of Y-PSZ $[10]$

1 μm . Electron backscatter diffraction patterns (EBSP) could be obtained without further preparation. The only problem was to find a matching geometry. As expected, the peaks were indexed as monoclinic or cubic/tetragonal. Examples are given in Fig. 16.6. Note that the cubic and tetragonal crystal structures of stabilized zirconia cannot be distinguished by EBSD. The crystal parameters may change continuously with the concentration of the stabilizer as mentioned above. Each state between cubic and tetragonal is possible. Thus, the resolution of EBSD is not sufficient as opposed to XRD [10].

Typical results of the EBSD phase analysis on polished cross sections are given in Fig. 16.7. The bimodal microstructure can be clearly recognized in the SEI image. It also appears in the phase map. The bigger particles were indexed as cubic/tetragonal zirconia (green), while the smaller particles consisted of monoclinic zirconia (red). The inverse pole figure (IPF) exhibits a random distribution of crystallographic orientation. The band contrast map also shows the bimodal structure. It represents the contrast at the observed diffraction bands in a greyscale. Thus, it illustrates the distribution of the local crystal perfection. The monoclinic grains exhibit a higher number of lattice defects than cubic/tetragonal grains. As stated in the introduction, the concentration of the stabilizer Y is not homogeneous. In particular, it is higher in the cubic/tetragonal grains than in the monoclinic ones. Hence the system is partially destabilized. As a result, the monoclinic fraction within the sample shows a variability in the local Y concentration [10].

After a FIB preparation of cross sections, a complete different phase composition was found. Corresponding results are presented in Fig. 16.8. As it can be seen in the SEI image, a tip was coated with platinum and then cut with 30 kV Ga⁺ ions at an angle of 90° relative to the Pt-coated surface. The beam current during the final polishing with an incident angle of 1° to the cut surface was 3 nA. Curtaining occurred due to inhomogeneity of the initial sample surface as well as of the Pt coating. This effect led to the dark lines in the band contrast map and also in the phase map. Surprisingly, the EBSD phase analysis showed a dense structure and clear diffraction patterns without much damage. The microstructure was completely cubic/tetragonal, in contradiction to the XRD and initial EBSD phase analysis on polished samples. The Yttrium distribution was comparable to the initial state, indicating that no further destabilization occurred. In order to explain this behavior, FIB milling and polishing were conducted on mechanically polished surfaces with different incident angle and energy of the ion beam [10]. Detailed phase maps and results are given by Berek et al. [10]. Identical areas of mechanically polished samples were scanned before and after additional FIB preparation with different ion energy and angle. A summary of the results is given in Table 16.1. The fraction of indexed points represents the ratio between the number of indexed points and the total number of points within the scan. The band contrast is a measure of the sharpness of the diffraction bands and also for the crystal perfection. The values of the band contrast can be compared if all diffraction patterns are taken under equal experimental conditions.

Differences in the initial states (from vibration polish) are attributed to local inhomogeneities. Note that after FIB with 30 kV, 30 nA and 5° incidence angle the fraction of indexed points rose while the fit and the band contrast were stable. The fit

Fig. 16.7 EBSD phase analysis on a polished surface of Y-PSZ. **a** SEI image of the analyzed area. **b** Phase map (green: cubic/tetragonal, red: monoclinic). **c** Inverse pole figure image. **d** EDX elemental distribution for Y. **e** Band contrast [10]

Fig. 16.8 EBSD phase analysis on a FIB cross section of Y-PSZ with the FIB parameters 30 kV and 3 nA. **a** SEI image. **b** Band contrast. **c** Phase map (green: cubic/tetragonal). **d** EDX elemental distribution for Y [10]

Table 16.1 Influence of FIB preparation on EBSD phase analysis of Y-PSZ [10]

	Monoclinic fraction	Fit	Fraction of indexed points	Band contrast (defined above in text)
	(Mol-%)	(°)	(%)	(–)
Vibration polished	21.1	1.05	38.4	3977
FIB (30 kV, 30 nA, 72°)	5.2	1.35	26.8	1772
Vibration polished	23.4	1.06	40.1	3962
FIB (5 kV, 4.8 nA, 72°)	2.0	1.21	34.0	3834
Vibration polished	35.8	1.03	43.1	4747
FIB (30 kV, 30 nA, 5°)	1.1	1.06	64.1	4501
Vibration polished	37.4	1.07	48.9	4380
FIB (5 kV, 4.8 nA, 5°)	34.0	1.06	49.7	3954

is defined as the medium difference of angles between all identified diffraction bands and the corresponding lattice planes of the crystal structure of interest. Obviously the structural transformation was followed by a crystal growth. FIB with 5 kV, 4.8 nA and 5° incidence angle led to nearly unchanged values. Thus, one can conclude that the influence of crystal damage at 5 kV is negligible. No amorphous layer could be

identified. Phase transformations in zirconia are connected with volume changes. However, no cracks were observed in the transformed regions.

16.3.2 MMC Foams

Open cell foam structures were produced with the aid of 30 pore per inch (ppi) polyurethane foam (pore size distribution in the range of 0.5 up to 3 mm) of size $50 \times 50 \times 20 \text{ mm}^3$ as templates [16–18].

One typical MMC foam is shown in Fig. 16.9. Three mixtures based on 100 vol% steel powder (0Z), 95 vol% steel/5 vol% Mg-PSZ-powder (5Z) and 90 vol% steel/vol% Mg-PSZ-powder (10Z) were mixed with organic additives. The manufacturing technology and the composition of the organic additives is described in [16–18]. The used process is one of the most promising manufacturing routes to produce open cell composite foams and is based on the patent of Schwartzwalder et al. [19]. It is a replication method using polyurethane sponge as a template.

In the given case the steel powder (Bitterfeld, Germany) had a mean particle size of $45 \text{ }\mu\text{m}$ and the ceramic powder (Saint Gobain, USA) had a mean particle size of $3.1 \text{ }\mu\text{m}$ respectively. Tables 16.2 and 16.3 give the corresponding chemical compositions.

The sintering conditions of the samples were 2 h at $1350 \text{ }^\circ\text{C}$ in Ar atmosphere. The in situ experiments were performed in a CT-ALPHA (ProCon X-Ray Garbsen, Germany), using a 160 kV transmission X-ray tube (Feinfocus Garbsen, Germany). High resolution X-ray absorption images were taken with a flat detector C7942SK-05

Fig. 16.9 Typical MMC foam [21]

Table 16.2 Chemical composition of the steel matrix in wt% [11]

C	Cr	Mn	Ni	Si	P	S	N	Fe
0.027	18.1	1.3	7.8	0.4	0.04	0.02	0.06	Bal.

Table 16.3 Oxide content of Mg-PSZ in wt% [11]

ZrO ₂	MgO	TiO ₂	Al ₂ O ₃	HfO ₂	SiO ₂	CaO
Bal.	2.84	0.19	0.5	1.85	0.07	0.2

(Hamamatsu, Japan). This detector has 2400×2400 pixels with a size of $50 \mu\text{m} \times 50 \mu\text{m}$ each on an area of $120 \text{ mm} \times 120 \text{ mm}$. The typical resulting spatial resolution (voxel size) within the sample was $15 \mu\text{m}$. The maximum possible sample size was always determined by the X-ray attenuation coefficients.

Loading plates of different geometries were used in order to enable full transmission of the samples without shadowing. The displacement was measured below the sample in the actuator. The deformation of the mechanical setup was found to be negligible. In the given case foam samples with a size of $10 \text{ mm} \times 10 \text{ mm} \times 20 \text{ mm}$ were investigated. The deformation speed was about 10^{-3} s^{-1} . The CT data were analysed with the software package VGSTUDIO MAX 2.1 (Volume Graphics GmbH Heidelberg, Germany). This program provides the possibility to calculate the exact position of the sample surface with a sub voxel resolution thus correcting the so called partial volume effect. The partial volume effect normally leads to undefined three dimensional surfaces because voxels on the sample surface belong partly to the sample and partly to the surrounding.

A typical result of this kind of sample surface calculation is given in Fig. 16.10. Note that there are pores inside the foam material. This is a result of the manufacturing technology. We assume that these pores are acting as weak areas during deformation. Therefore they are included in the calculation of the total sample surface. Based on the defined surface of the foam including the surfaces of pores, cell wall thicknesses can be calculated. This is realized by the determination of shortest distances between nearest surface areas within a search angle of 30° . Triple points of the foam cells always have a higher thickness than single cell walls due to surface tension effects of the slurry used. As a result of the manufacturing process pores are located mainly in the triple points. This is connected with weak points. Therefore the cell wall thickness at pores is included in the analysis.

Figure 16.11 shows typical stress-strain curves for a steel—5 vol% zirconia composite. Three areas are clearly visible. Following DIN 50134 [22] there are different ranges for the compressive stress (elastic deformation, cracking, densification) they can be separated using different ranges for the compressive stress R where R_{100} is the stress in the plateau:

(R_x : $x = x\%$ of plateau stress R_{pland} the foam respectively. Ourt; R_{plt} = average value of stresses between $e_d = 20\%$ and $e_d = 40\%$; $e_d = \text{strain}$ [22]).

1. Elastic deformation between R_{20} and R_{70}

Fig. 16.10 Reconstructed cross section [11]

Fig. 16.11 Stress strain curves of three foams [11]

2. Cracking leading to a plateau between R_{70} and R_{130}
3. Densification leading to a significant increase above R_{130} .

Note, that there is a large scatter in the data. The cell wall thickness is inhomogeneous within the sample depending on the inhomogeneity of the starting materials and the manufacturing technology.

Results of a stopped in situ experiment are shown in Fig. 16.12.

Fig. 16.12 Scheme of a stopped in situ deformation experiment and calculated sections for 0, 10 and 20% strain [11]

The compression was stopped after 2, 4, 6, 10 and 20% compressive strain respectively. After stopping the deformation process stress relaxation occurred. This is connected with a significant dropdown of the compressive stress within a few minutes while the compressive strain was held constant. After this period an equilibrium state is reached. The maxima in the curves of the compressive stress correspond to the curves in Fig. 16.11. XCT scans were taken in the equilibrium state under constant stress. In order to show deformation processes with a sufficient spatial resolution, defined regions of interest were considered. In the case of Fig. 16.12 calculated 3D pictures of thin layers taken at the same position of the sample after 0, 10 and 20% compressive strain are shown. First cracks appear at the weakest cells. These are cells of a rather big size, a small cell wall thickness and an extension perpendicular to the deformation axis. A localized damage is clearly visible. Starting point in deed are smaller cell walls. As can be seen in Fig. 16.13, there is a typical deformation band starting from the area of first cracks.

For the deformation of MMC foams under compressive stress in agreement with the literature three regimes were found: elastic deformation, plastic collapse and densification. The normalized deformation maps given by Ashby [23] show the principal behaviour of the stress strain curves in dependence on the densities of the bulk material of the foam and the foam respectively. Our results confirm this view. The data are shifted slightly to smaller compressive stress values. As Elliott [24] found

Fig. 16.13 Reconstructed cross section after 20% compression [11]

for polyurethane foams the compression of MMC foams also lead to the cooperative collapse of connected cells. Note that the foams of the given study were manufactured by the replica technique on the base of polyurethane foam (as shown in Chap. 1 of this volume). We observed deformation bands arising in regions of smaller cell wall thicknesses. Singh [25] found this kind of anisotropy in open celled Ti foams. The deformation was dependent on size, shape and orientation of the cells under consideration. Obviously deformation bands start at bigger cells with a small cell wall thickness and some extension perpendicular to the deformation direction. The rising of this kind of deformation bands can be explained by the dramatic change of the stress distribution in the neighbouring cells after the first brake of a cell wall. The correlation between local deformation and local phase composition was investigated by Berek et al. [21].

Figure 16.14 shows the result of a digital volume correlation calculation. The gradient magnitude is a measure of the local deformation. Thus, region 3 shows maximum deformation. Figure 16.15 exhibits a typical cross section of this region as the result of a local preparation process with its correspondence to the reconstructed XCT image. Local phase analyses of a number of particles like the one in Fig. 16.16 lead to the results in Fig. 16.17.

Note, that the transformation from the cubic structure to the tetragonal one is a continuous deformation process in dependence on the local concentration of stabilizers as was shown in [26]. Thus, the distinction between cubic and tetragonal zirconia is not possible by EBSD. However, it becomes clear, that the regions of high deformation (c.f. Fig. 16.14) correspond to regions of pronounced phase transformation (Fig. 16.17).

Fig. 16.14 Overlay of the slice of a reconstructed 3D image (background) and the gradient magnitude of the deformation field (highlighting) with defined regions of interest after 20% compressive deformation in the Z direction [21]

Fig. 16.15 Correlation between a reconstructed 2D image and the corresponding cross section after 20% compression in the Z direction. **a** Photograph of the cross section. **b** 2D slice from the reconstructed 3D image [21]

Fig. 16.16 EBSD analysis of a zirconia agglomerate after 20% compression in the Z direction. **a** EDS image. **b** Kernel average misorientation map for the steel matrix. **c** Band contrast map. **d** Phase map (green: monoclinic zirconia; red: cubic/tetragonal zirconia; orange: austenite; blue: α' -martensite; yellow: ε -martensite; white: points not indexed) [21]

16.3.3 MMC-Honeycomb Structures

The manufacturing technology of honeycomb square cell composites is based on the well-established extrusion technique [27, 28] and is described in Chap. 5 of this volume. Before extrusion the inorganic powder materials were mixed within 30 min in a tumble drum with yttria stabilized zirconia balls. In a second step the plasticizers and binders were added and the material was further mixed in a conventional mixer (Toni Technik, Germany) for 5 min. Finally, water was added and the recipes were kneaded until a homogeneous and plastic paste was achieved. Due to a combined de-airing single screw extruder with vacuum chamber and sigma kneader type LK III 2A (LINDEN, Germany) honeycomb structures were extruded with a square

Fig. 16.17 Box plots of the distributions of monoclinic zirconia fractions at different states and in different regions showing the 25th percentiles at the lower edges and the 75th percentiles at the upper edges [21]

Table 16.4 Chemical composition of the steel matrix in wt%

C	Cr	Mn	Ni	Si	Mo	N	Fe
0.031	16.2	7.1	5.9	1.12	0.06	0.011	Bal.

Table 16.5 Chemical composition of Mg-PSZ zirconia powder in wt%

ZrO ₂	MgO	SiO ₂	HfO ₂	Al ₂ O ₃	TiO ₂
Bal.	3.4	2.4	1.7	0.6	0.1

shape of $25 \times 25 \text{ mm}^2$ and a honeycomb structure of 14×14 channels (200 cpsi—channels per square inch). After extrusion the specimens were dried stepwise at 40–80–110 °C in an air-circulated dryer within 12 h at each temperature and decreasing humidity from 80 to 20%. Afterward cubic samples of 25 mm length were cut and placed on alumina tiling. The debinding step took place at 350 °C for 90 min in air atmosphere with a heating rate of 1 K/min. To prevent oxidation effects during further heat treatment the honeycombs were placed with stock in graphite crucibles after debinding. Finally the samples were sintered pressure less in a 99.999% argon atmosphere using an electrical furnace type HT 1600 GT Vac (LINN, Germany) with oxidic furnace lining and MoSi₂ heating elements. After heating with 5 K/min the temperature of 1350 °C was kept constant for 120 min followed by cooling with 10 K/min to room temperature. Open porosity and bulk density were determined based on Archimedes principle and DIN EN 1389 with toluol as immersion fluid [27]. In the given case 10 vol% of Mg-PSZ powder was mixed with TRIP-steel powder. The chemical compositions are given in Tables 16.4 and 16.5.

In order to perform in situ compression experiments in an XCT, samples with 2×2 channels were used. Figure 16.18a, b show corresponding photographs.

Fig. 16.18 Extruded MMC honeycomb structure (a) and samples for in situ experiments under compressive load in an XCT (b)

The experiments were performed in a CT-ALPHA in the same procedure as shown for the foams. The typical resulting spatial resolution (voxel size) within the honeycomb sample was $10\text{ }\mu\text{m}$. A specially constructed load frame from Hegewald & Peschke Measuring Technology Nossen, Germany, was used. Two loading plates are positioned in a carbon fibre reinforced polymer tube between the top load cell and the bottom mechanical actuator. The deformation speed was about 10^{-3} s^{-1} .

The CT data were analysed in the same way as mentioned before with the software package VGSTUDIO MAX 2.1 from Volume Graphics GmbH Heidelberg, Germany. Within previous work ex situ compressive out of plane deformation experiments on honeycomb structures based on Austenitic stainless steel AISI 304L were performed [1, 2, 27, 29]. As a result of EBSD phase analysis it was concluded that stress induced martensitic phase transformations of metastable tetragonal zirconia to the stable monoclinic structure occurred below 10% of compressive strain [27, 29]. A rather high amount of the monoclinic phase (>80%) was observed in the as sintered state. The reason for this behaviour was found to be destabilisation due to diffusion of magnesium and the formation of grain boundary precipitations at sintering temperature and during subsequent cooling.

The most important differences to the present work are the composition of the steel alloy used and the performance of quasi in situ deformation in the XCT. The steel alloy 16-7-6 has a significantly higher amount of manganese while the nickel content was slightly reduced. Figure 16.19 shows typical deformation curves of MMC samples (see Fig. 16.18b). Force and deformation were measured directly. The real sample cross section area was determined using wall thicknesses, which were calculated on the base of the XCT-scans.

The geometrical dimensions of the samples were $3.5 \times 3.5 \times 6\text{ mm}^3$ with cell wall thicknesses of about 0.37 mm. After linear elastic deformation there was a broad range of plastic deformation with typical strain hardening. This strain hardening is a superposition of both martensitic transformation processes of steel and zirconia. The

Fig. 16.19 Deformation curves of MMC honeycombs under compressive load in out of plane direction [12]

Fig. 16.20 XCT images of MMC honeycombs at different levels of compressive strain [12]

expected deformation behaviour of such kind of square celled honeycombs is torsion-flexural buckling of the cell walls [30] followed by a progressive folding process [6, 31, 32]. For stresses higher than the so called bifurcation stress the structure becomes instable and a softening is observed [30, 33]. In the given case this bifurcation stress is close to the maximum compressive stress. During the deformation process the X-ray absorption picture can be observed directly. In every case the first cracks occurred immediately after passing the maximum. Figure 16.20 gives typical XCT results. Sections were calculated at the same sample position but different levels of deformation thus allowing the study of the deformation behaviour directly.

The deformation is still in the plastic range without breaking of the walls. The sections show a porous region in the middle. Buckling is observed after 30% compression. These results are in correspondence with [14]. The investigation of the deformation behaviour of cruciform honeycomb MMC-samples (as seen in Fig. 16.20 but without the outside wall) within the XCT showed that cruciform MMC-specimens underwent a plastic deformation with irreversible torsion and warping actions. Even small imperfections, particularly piercing defects in the cell walls, had an effect on their critical bifurcation. After finishing the XCT scans, samples we prepared for the EBSD phase analysis. After embedding in epoxy, they were carefully polished. As a result, one can directly compare the calculated XCT sections with the polished sample areas. A minimum of 10 sample areas was scanned by EBSD thus enabling the study of the distribution of the phase composition. The agglomerates of zirconia typically contain a cubic/tetragonal core in a monoclinic body. Note that the lattice parameters of cubic and tetragonal zirconia differ only about 2%. Thus the resolution of EBSD is not sufficient to distinguish these structures. Furthermore there are intermediate metastable states. The lattice parameters can be directly related to the magnesia concentration [26]. Nevertheless the monoclinic structure can be clearly distinguished from the cubic/tetragonal structure by EBSD and the martensitic tetragonal-monoclinic transformation is responsible for transformation toughening. Hence, the determination of the monoclinic phase content is essential. Figure 16.21 gives the corresponding results.

These box plots exhibit minima, maxima and the 25, 50 and 75% percentiles of the corresponding distributions of the measured monoclinic phase fractions. Obviously similar to earlier investigations there is a considerable phase transformation during sintering and subsequent cooling. However the change is much smaller in this study in comparison to earlier studies with low manganese alloyed steels [8, 29]. In the as sintered state the value for the 25 percentile is about 60% of monoclinic zirconia. That

Fig. 16.21 Box plots of the distributions of monoclinic zirconia fractions at different states and in different regions showing the 25th percentiles at the lower edges and the 75th percentiles at the upper edges of the boxes [12]

means a remarkable amount of metastable zirconia for phase transformation is left. The range between 0 and 10% of compressive strain was investigated in more detail because earlier investigations show, that most of the phase transformation occurred in this region. However, in the present case the phase distribution stays stable up to 30% of deformation. This effect can be related to the higher manganese content of the steel alloy used. Mn^{2+} stabilizes metastable zirconia in a similar way as Mg^{2+} [34, 35]. On the other hand manganese forms precipitates with silicon and aluminum like magnesium thus acting as a competitor. In the end there is less diffusion of magnesium out of the zirconia and some diffusion of manganese into the zirconia thus stabilizing the metastable phases. Most of the stress-assisted phase transformation takes place between 30 and 40% of compressive deformation. Obviously, the stress limit for the phase transformation in Mn stabilised zirconia is much higher than in Mg stabilised zirconia. It is in the range of the stress maximum of the stress-strain-curve.

16.3.4 Composite Beads with Graded Layer Structures

The manufacturing technology of the composite beads is based on an alginate gelation and described detailed in Chap. 1 of this volume. Beads with graded layer compositions were prepared using a gel-casting process by alginate gelation. The used method is based on the gelation of sodium alginate in direct contact with calcium ions in an aqueous solution as solidifying agent. The used sodium alginate serves as gelation agent. During the forming process, alginate and bivalent ions react by attracting each other's molecular chains and the transition of water-soluble Na- to water-insoluble Ca-alginate takes place. Suspensions for the fabrication of composite beads with graded layer structures were prepared from austenitic stainless steel powder (TLS Technik, Germany) and magnesia (3.25 wt%) partially stabilized zirconia (Saint Gobain) [13].

The core of the beads consists of a mixture of 90% steel-powder and 10% zirconia powder and are coated with a slurry of 95% steel-powder and 5% zirconia powder. The outmost layer consisted of 100% steel. To get an overview about the complete bead, an investigation in XRM (Versa X-ray microscope) with a voxel size of 1.1 μm was conducted. The bead was fixed on a block of Si_3N_4 . No additional preparation of the bead was necessary. Figure 16.22a shows a section through the reconstructed volume. Three essential components which are the steel matrix, ZrO_2 -particles/agglomerates with precipitations and pores can be distinguished in the particle section. The study with the XRM proves the result of SEM that there are no gradation zone and no cracks between the different layers. The histogram during measurement shows an asymmetric peak of absorption. This impulse edge to higher absorption coefficients. This impulse edge can be traced back to ZrO_2 . Therefore, the different areas were coloured based on the histogram. As a result, the position of ZrO_2 within the (less absorbing) steel matrix can be distinguished. It is particularly clear that the surface layer does not contain ZrO_2 . Further tests were performed to show if a higher image resolution can be reached using the

Fig. 16.22 Reconstructed cross section based on a XRM-scan of MMC bead sample; grey: austenite; light grey: ZrO_2 and precipitations; black: pores resp. ambient; **a** XRM-scan of a volume part of MMC sphere using a Zeiss Xradia 510 Versa, **b** position of part c in the volume, **c** reconstructed cross section (grey: austenite, light grey: ZrO_2 and precipitations, black: pores resp. not indicated) [13]

Zeiss Xradia 510 Versa. Therefore a high resolution scan with a $20\times$ -objective for large optical magnification was performed. A pixel size of $0.41\text{ }\mu\text{m}$ using a camera binning of 2 (2×2 pixels are averaged and combined to one) was reached. Figure 16.22a–c illustrates the reconstructed cross section of a part of the volume. The Zeiss Xradia 510 Versa enables different types of drift corrections. Besides the default thermal drift correction of the X-ray spot on the tungsten target, a mechanical sample drift correction can be applied which takes into account the unwanted movement of the sample. With respect to the appearance of different drift phenomena, the reconstruction required the use of an additional binning 2. Thus, the voxel size of the reconstructed volume results in about $0.8\text{ }\mu\text{m}$. Nevertheless, a surface zone free of ZrO_2 can be observed [13].

Additional to the XRM-scans of the beads after sintering, XRM-scans of deformed beads were performed. The goal was to show potential differences in crack initiation and crack morphology after deformation by uniaxial compressive loading. Layered beads (Bead a), particle reinforced beads with 90 vol% steel and 10 vol% zirconia (Bead b) as well as pure steel beads (Bead c) were tested. Figure 16.23a–c shows reconstructed cross sections of these three different beads after deformation up to 20%. The voxel size of the reconstructed volumes is $2.2\text{ }\mu\text{m}$. As it was found for the XRM-scan of the MMC bead sample, the histogram comprises an asymmetrical peak of absorption. There is a wide impulse edge to higher absorption coefficients which is related to ZrO_2 . Therefore, the different areas were coloured in the histogram, plotted in yellow. As a result, the position of ZrO_2 within the (less absorbing) steel matrix can be illustrated. Figure 16.23a shows a boundary zone free of zirconia, whereby Fig. 16.23b illustrates a regular distribution of zirconia particles. The crack initiation into the specimens was of major interest. Therefore, cross sections in the area of maximal crack width were chosen. The sample surface is marked in white. It can be seen in the cross sections that the crack in sample a (graded layer bead) does not reach the bead's centre. Bead b (90 vol% steel + 10 vol% zirconia) shows a greater crack propagation. The crack in sample c (pure steel bead) nearly reaches through the complete sample. As expected, the crack initiation starts at the surface

Fig. 16.23 **a–c:** Reconstructed cross sections in x-y-plane with maximal crack length. **a** graded layer bead; **b** 90 vol% steel and 10 vol% zirconia; **c** pure steel bead; blue: steel matrix; yellow: zirconia particles; white: surface marks; **d–f:** Reconstructed volumes with crack in y-plane; **d** graded layer bead; **e** 90 vol% steel and 10 vol% zirconia; **f** pure steel bead [13]

in the range of maximal tension. Figure 16.23d–f illustrates these areas in side view. Sample a (graded layer bead) shows an incipient crack while the other beads present continuous cracks. All pictures of XRM illustrate a very good gradation between the different layers and no detachment of the coating. Further studies with in situ-CT load cells are planned to verify the findings and show the mechanism of failure [13].

16.4 Conclusions

Within this work the target preparation for an optimal EBSD and XCT analysis of composites was investigated and furthermore MMC foams and honeycombs were examined. Focused ion beam preparation is a very helpful tool for producing polished cross sections of defined regions in inhomogeneous samples with complicated shape. The different aspects of the interaction between the ion beam and the sample should be considered. In case of metastable Y-PSZ and Mg-PSZ, phase transformations were observed after FIB preparation with 30 kV, 30 nA and 5° incidence angle. Damage was the dominating effect for angles of 72°. The expected local temperature increase due to the ion bombardment (30 kV, 30 nA) is about 700 K for ZrO_2 . Thus, the observed phase transformations could be explained on the basis of the increased temperature (700 K) in the corresponding Y-PSZ phase diagram. In case of Mg-PSZ, the transition temperature is 1083 °C. The local temperature rise was obviously lower. The excitation energy for the observed phase transformation was smaller than expected from the phase diagrams of the thermodynamic equilibrium. Using 5 kV, 4.8 nA and 5° incidence angle no phase transformations and no damage were observed. Thus, these conditions are suited for the FIB preparation of metastable zirconia [10].

An experimental setup for in situ investigations under compressive stress in a laboratory XCT was developed and successfully tested. Complete deformation curves can be taken. The size of the samples is limited due to the transferability. Nevertheless the results for MMC foams based on TRIP-steel and Mg-PSZ correspond to results on rather bulk samples investigated by a conventional testing machine. XCT scans can be taken in the frame of stopped in situ experiments. In this way the deformation behavior of defined sample regions can be investigated. Thus interrupted in situ experiments as described by Berek et al. [11] are well suited to investigate the deformation behavior of foams and other samples which are transferable for the X-rays used. For the deformation of MMC foams under compressive stress three regimes were found in agreement with the literature: elastic deformation, plastic collapse, and densification. The deformation was dependent on size, shape and orientation of the cells under consideration. Obviously deformation bands start at bigger cells with a small cell wall thickness and some extension perpendicular to the deformation direction. The occurrence of this kind of deformation bands can be explained by the dramatic change of the stress distribution in the neighbor cells after the first brake of a cell wall [11].

Furthermore the experimental setup for interrupted in situ investigations under compressive load in a laboratory XCT up to 100 kN load was developed and successfully tested to demonstrate that the crush resistance and equally the energy absorption capability of cruciform TRIP-steel structures (honeycombs) are improved by the addition of 10 vol% of Mg-PSZ. The strain hardening of the composite material can be explained by the combined effects of particle reinforcement and martensitic phase transformations in the TRIP-steel and the Mg-PSZ reinforcement at the same time. The XCT investigations showed that the cruciform specimens underwent a plastic deformation with irreversible torsion and warping effects. The composite specimens exhibit a higher initial compressive peak stress followed by structure softening and the formation of an expanded plateau region. Even small imperfections, particularly piercing defects, in the honeycomb's cell walls had an appreciable effect on their critical bifurcation load. An accelerated inhomogeneous buckling in the flange edge regions was observed in case of cruciform samples. On the basis of these experimental studies, the characterization of the deformation and failure behavior of the honeycomb structures or comparable cellular materials by analytical modeling can be promoted [14].

With the aid of XRM and X-ray CT it was possible to examine and evaluate layered composite beads. To show potential differences in crack initiation and crack morphology after deformation by uniaxial compressive loading XRM scans of deformed beads were performed. All pictures show the perfect layer formation and the crack initiation starts at the surface in the range of maximal tension.

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