MS43-P11 Formation and high-temperature stability of metastable $(Cr,Zr)_2O_3$/$(Zr,Cr)O_2$ nanocomposites

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Successive crystallization of amorphous Cr-Zr-O thin films, formation of the $(Cr,Zr)_2O_3$/$(Zr,Cr)O_2$ nanocomposites and thermally induced changes in the hexagonal crystal structure of metastable $(Cr,Zr)_2O_3$ were investigated by means of in situ high-temperature synchrotron diffraction experiments up to 1100°C. The thin films of Cr-Zr-O were deposited at room temperature using reactive ion beam sputtering from zonal Cr-Zr targets under oxygen flow. The resulting amorphous Cr-Zr-O solid solutions contained up to 15 at.% Zr. During the annealing in vacuum, the Cr-Zr-O solid solutions decomposed into two metastable phases, Cr-rich $(Cr,Zr)_2O_3$ and Zr-rich $(Zr,Cr)O_2$, which crystallized in hexagonal and tetragonal structure, respectively. With increasing Zr content in amorphous Cr-Zr-O, the start of the phase segregation and crystallization was shifted from 600°C at 3 at.% Zr to 1000°C at 15 at.% Zr. With the aid of the in situ high-temperature synchrotron powder diffraction experiments, it was found that the metastable $Cr_{2-2x}Zr_xO_{3-x}$ can accommodate up to approx. 3 at.% Zr. The zirconium atoms occupy partially the Wyckoff positions 6b in the corundum-like crystal structure of Cr_2O_3 that are empty in the stoichiometric chromium oxide. The incorporation of Zr into the crystal structure of Cr_2O_3 inflated the elementary cell and modified the thermal expansion of $Cr_{2-2x}Zr_xO_{3-x}$. The tetragonal structure of zirconia was stabilized by chromium. The phase segregation during the crystallization led to the formation of $(Cr,Zr)_2O_3$/$(Zr,Cr)O_2$ nanocomposites. The size of crystallites in these nanocomposites decreased with increasing Zr content from 60 nm to 30 nm and increased only slightly at the highest annealing temperatures. In summary, this contribution illustrates the microstructure design in nanocomposites on the example of metastable chromium and zirconium oxides.

Keywords: Cr-Zr-O nanocomposites, in situ high-temperature synchrotron diffraction, metastable Cr(2-2x)Zr(x)O(3-x)

MS43-P12 Structural response of melt-spun poly(3-hydroxybutyrate) fibers to heat and stress investigated by wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS)

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Poly(3-hydroxybutyrate) (P3HB) is produced by bacteria as intracellular carbon and energy storage compound. P3HB is sustainable, biocompatible and biodegradable, and it qualifies for the use in numerous textile and medical applications due to its exceptional properties as well as reasonable production costs via a relatively simple biosynthesis process. The brittleness of native P3HB and its rapid thermal degradation at temperatures just above the melting temperature, however, makes melt-spinning of P3HB into fibers a challenging task. The issue has been previously addressed in the scientific literature, but at the laboratory scale only, and up to now, melt-spinning of P3HB at large scale is not feasible.

By performing studies regarding the effects of additives and of modifications of the draw-off unit on the melt-spinning performance of P3HB, we succeeded in developing an upscalable melt-drawing method for P3HB fibers, leading to fibers exhibiting promising tensile strengths up to 215 MPa.

In the equatorial 2Theta scan of the WAXD patterns of these fibers, we observed a series of local maxima and postulated a highly ordered amorphous phase, which is kinetically trapped between the aligned lamellae of the crystalline α-phase [1]. This is in contrast to the previous literature, where diffraction signals in this region are commonly described as one reflection, assigned to the so-called "β-form" of P3HB. In our model, the local maxima in the 2Theta scan correspond to preferred distances between polymer chains that are oriented nearly parallel to, but irregularly arranged along the fiber direction.

For the present study, P3HB fibers are subjected to various tensions and temperatures. The intensities of the highly oriented (020) and (110) reflections, e.g., decrease with increasing tension (Fig.1). Simultaneously, the intensity of the reflections assigned to the highly ordered amorphous phase is considerably increasing. Cyclic change of load reveals a high degree of reversibility for these phenomena, which supports our model of the highly ordered amorphous phase described above. This and more results of *in-situ* WAXD and SAXS experiments to trace the structural response of the P3HB fibers will be presented.

[1] Hufenus R, Reifler FA, Fernandez-Ronco MP, Heuberger M. Eur Polym J. 2015; **71**:12-26.

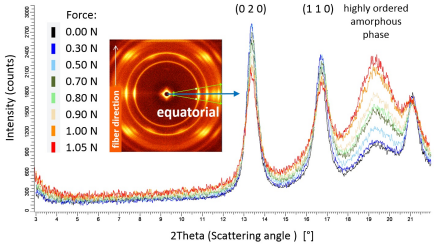

Figure 1. Structural response of a P3HB fiber to increasing tensional forces. 2Theta scans of equatorial sectors in the WAXD pattern. Under load, the orientation of the amorphous phase is enhanced, to the disadvantage of the orientation in the crystalline phase.

Keywords: fiber, melt-spinning, biopolyester, biopolymer, wide-angle X-ray diffraction, WAXD, small-angle X-ray scattering, SAXS

MS43-P14 STOE InSitu HT2 – a new in-situ reaction chamber in Debye-Scherrer geometry

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STOE & Cie GmbH in Darmstadt, Germany, has developed a new equipment for their STOE STADI P powder diffractometer series, the InSitu HT2. This new reaction chamber in Debye-Scherrer geometry is mounted on a vertical setup Goniometer with Mo $K\alpha_1$ radiation and offers the user a horizontal capillary with up to 2mm inner diameter to expose the sample to high temperatures up to 1600 K and a gas flow through the capillary of 10 - 100 ml/min.

The sample volume is in the area of some mm^3, only, offering real micro sample investigations under non-ambient conditions and reactive gases. First test measurements with a carbon coated Pt – Ru catalyst [1] under oxygen atmosphere at T from RT – 300°C showed impressively that the STOE InSitu HT2 fills a gap in the field of commercial available in-situ cells in transmission geometry.

Figure 1 shows the appearing RuO_2 reflections with those of the Pt-Ru alloy and the carbon matrix.

[1] C. Roth, N. Martz and H. Fuess., *Phys. Chem. Chem. Phys.*, **2001**, *3*, 315-319.

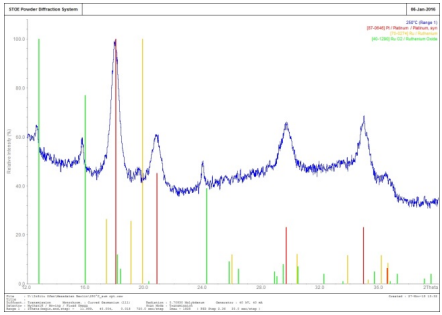

Figure 1. X-ray pattern at 250° (blue) with the markers for Pt (red), Ru (yellow), and RuO_2 (green)

Keywords: XRPD, non ambient methods, X-Ray diffraction, in situ measurements, reaction chamber