doi: 10.1017/S1431927609095397
Microsc Microanal 15(Suppl 2), 2009

Crystallization Kinetics of Amorphous Alumina-Zirconia-Silica Ceramics

T. Chráska,* J. Hostomský,** M. Klementová,** and J. Dubský*

* Institute of Plasma Physics of the ASCR, v.v.i., Za Slovankou 3, 182 00 Prague, Czech Republic
** Institute of Inorganic Chemistry of the ASCR, v.v.i., 250 68 Husinec-Řež 1001, Czech Republic

Nanocrystalline ceramics has a wide potential of applications due to its significantly improved properties such as hardness, strength, abrasion resistance and toughness. Even though nowadays ceramic nanopowder can be conventionally synthesized in large quantities, the consolidation of nanoparticles into mesoscopic structures and large bulk pieces remains a challenge [1]. In the alternative approach such as plasma spraying, the powder compaction step is completely avoided by producing amorphous material by rapid solidification, which can then be thermally treated to introduce nanocrystalline structure by controlled crystallization [2].

Crystallization kinetics of amorphous alumina-zirconia-silica ceramics was studied for seven different material compositions (labeled as NZ, A, B, C, E, F in Fig. 1) based on the bulk cast ceramic material called Eucor^{TM} [3]. The amorphous materials were prepared by plasma spraying thus the samples consist of thin splats with a significant chemical variation due to different proportions of Al and Zr oxides in the individual particles of injected powder. Each individual amorphous splat in the as-sprayed materials is, however, chemically homogeneous.

The amorphous materials crystallize above 920ºC primarily as tetragonal ZrO_2 solid solution with Al_2O_3 and to a small extent as δ-Al_2O_3 in Al_2O_3-rich splats. The tetragonal zirconia nanocrystallites have average diameters increasing from 10 to 23 nm with increasing silica content (Fig. 2). For silica containing materials the nanocrystallites are embedded in silica rich remains of the amorphous matrix thus creating steep concentration gradients at the nanocrystal/glass interface. The kinetic stabilization of the nanoscale microstructure is related to the silica rejection during growth involving a soft impingement between neighboring nanocrystallites. Based on DSC measurements, the apparent activation energy of the crystallization increases approximately from 900 to 1500 kJ/mol with decreasing silica content. According to the values of Avrami coefficient and on the microstructural observations, crystallization mechanism of the silica containing materials is best described by instantaneous nucleation followed by three dimensional crystal growth controlled by diffusion transport of Zr and Si cations in opposite directions (demixing). The Avrami exponent for the NZ material, however, points to a three dimensional growth mechanism controlled by a reaction at the phase boundary.

References

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[4] This work was carried out under the ‘‘Nanotechnologies for Society’’ program, supported by project no. KAN300430651 administered by the Academy of Sciences of the Czech Republic.

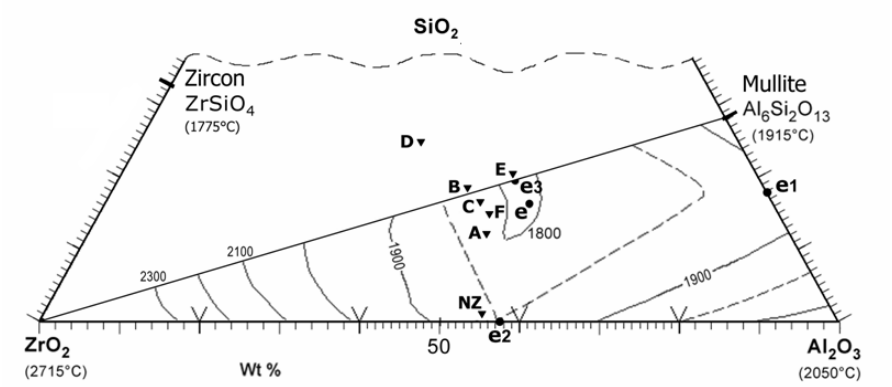

FIG. 1. Part of ternary equilibrium phase diagram showing different compositions of materials used in this study (marked by triangles). e1, e2, e3 – binary eutectic points, e - ternary eutectic point.

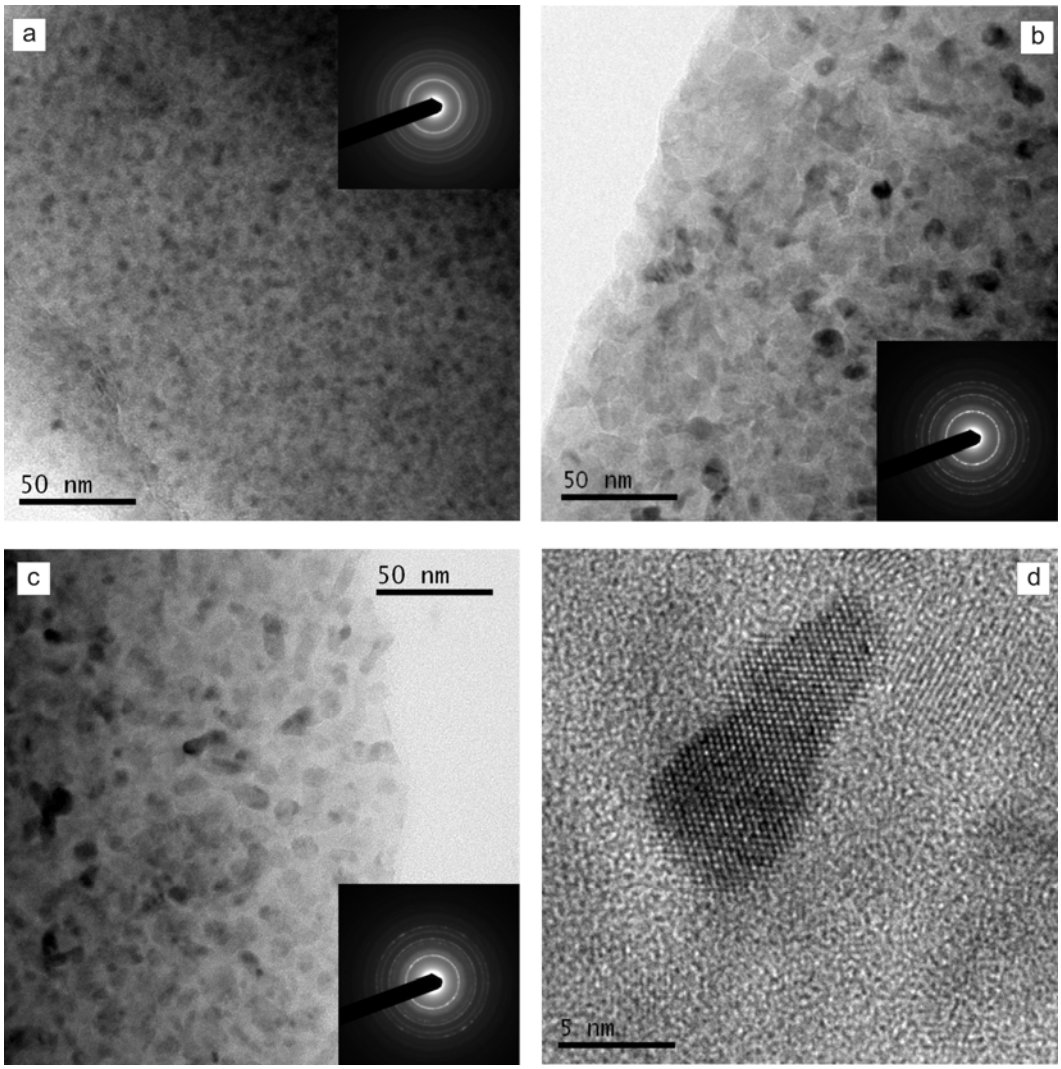

FIG. 2. Bright field TEM and HRTEM micrographs of annealed samples with corresponding diffraction patterns shown as insets. a) NZ, b) A, c) D, and d) a high resolution image of a tetragonal ZrO_2 nanocrystal embedded in a weak contrast amorphous phase.

https://doi.org/10.1017/S1431927609095397 Published online by Cambridge University Press