An effective strategy to inhibit grain coarsening: Construction of multi-element co-segregated grain boundary complexion

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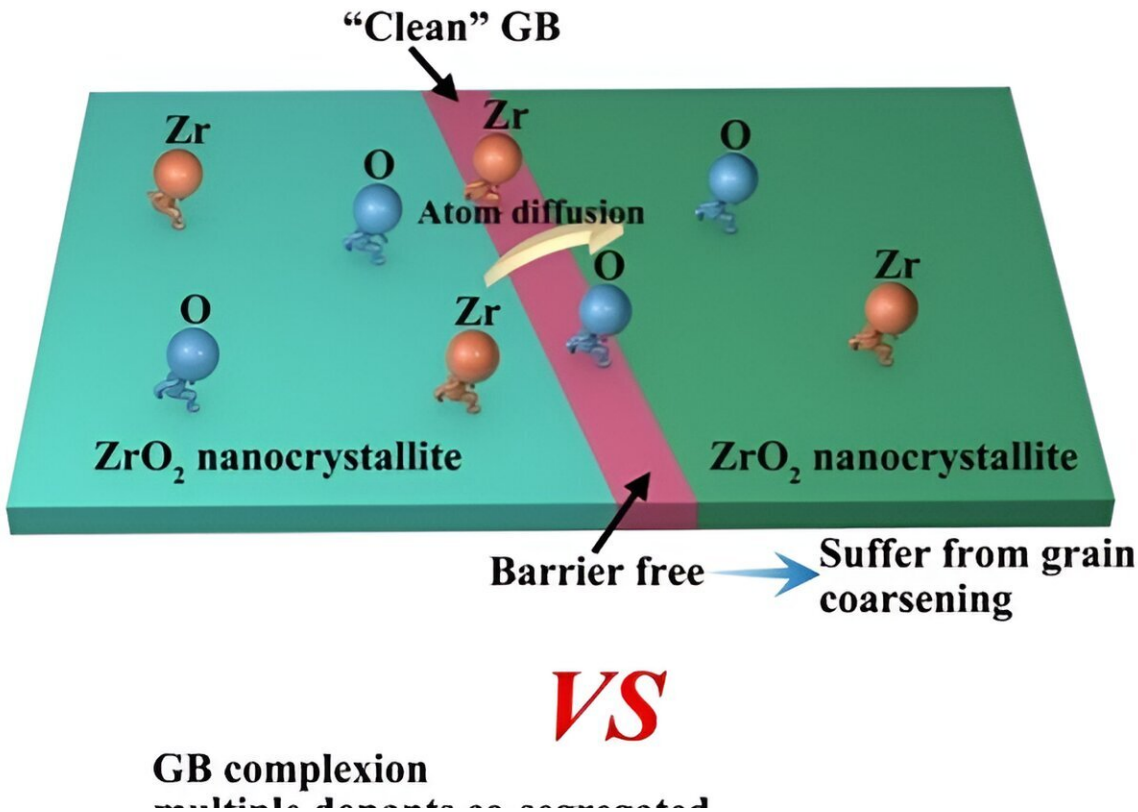

In un-doped ZrO_2-SiO_2 system, the GBs between ZrO_2 nanocrystallites were clean without dopant segregation. When heating the material, Zr and O atoms could easily cross the GBs, resulting in grain coarsening. In comparison, when multiple dopants were added to the material system, GB complexions with multiple dopants co-segregated were formed. The GB complexions acted as a barrier for atom diffusion, which effectively hindered grain coarsening. The

microstructure and chemical composition of the GB complexions were carefully characterized by advanced electron microscopy techniques. These findings are important for understanding the GB complexions and are expected to provide new insights to design nanomaterials with excellent thermodynamic stability. Credit: Journal of Advanced Ceramics, Tsinghua University Press

To date, ceramic scientists have devised various strategies to impede grain coarsening. The utilization of nano-sized precursor powder can not only facilitate the densification process, but also yields bulk ceramics with reduced grain sizes compared with micron-sized precursor powder.

Rapid sintering bypasses the low-temperature surface diffusion stage and directly enters the high-temperature sintering stage through rapid heating, rendering it an effective way to inhibit grain coarsening. However, these aforementioned strategies fail to prevent coarsening during the application of nano-ceramics in medium- or high-temperature environments.

The introduction of the secondary phase can also enhance thermal stability of nanograins. By pinning grain boundaries (GBs) and reducing their mobility, the secondary phase effectively inhibits coarsening. However, it is challenging to achieve a uniform distribution of the secondary phase, which may cause detrimental effects on other properties.

Solute segregation in GBs has been shown to reduce GB energy and weaken the driving force of grain growth. Nevertheless, most reported studies have only investigated the addition of one or two types of solute atoms, limiting the extent of GB energy reduction. Therefore, further exploration is needed to fully understand and harness the potential of solute segregation as a strategy.

Recently, a team of material scientists led by Le Fu from Central South University, China proposed an effective strategy to inhibit grain coarsening by constructing GB complexions with multiple dopants co-segregated. The team published their work in Journal of Advanced Ceramics on March 28, 2024.

As a demonstration of the feasibility of the strategy, multiple selected dopants were doped to a ZrO_2-SiO_2 nanocrystalline glass-ceramic (NCGC) to form GB complexions. The microstructure of the GB complexions with multiple dopants co-segregated was characterized. Meanwhile, the underlying mechanisms of the effects of GB complexions on inhibiting coarsening were discussed.

In this report, the researchers aimed to construct a multi-element co-segregated GB complexion. The first as well as the most important question is to select the dopants. It has been proved that GB segregation is largely affected by the ionic radius and valence state of both dopant cations and the host one. For dopant ions that have large ionic radius mismatch (ε) with the host Zr^{+4} ion (84.0 pm), they would be pushed to the GBs, instead of dissolving in ZrO_2 lattices.

In addition, ZrO_2 GBs are positively charged, and dopant ions with valence states lower than +4 can form a negative space charge cloud at the GBs, which could also enhance the GB segregation tendency of the dopant ions. Taking the above two criteria into consideration, the researchers selected five dopant ions, i.e., Cs^{+}, Ba^{+2}, La^{+3}, Ca^{+2}, Al^{+3} ions. They all had large ε with the host Zr^{+4} ion and their valence states were lower than +4.

Hence, theoretically, they should co-segregate at the ZrO_2 GBs." said Fu, associate professor at School of Materials Science and Engineering at Central South University (China), an expert whose research interests focus on the field of ceramics.

"We characterized the GB complexions with TEM techniques and found that Y, Ca, Ba, and La elements showed significant segregation at the GB complexion with a thickness of 2.5 nm. Meanwhile, lattice fringes were formed at the GB complexion, indicating that the GB complexions were crystalline superstructures. In addition, we also obtained a full 3D reconstruction of GB complexions on the atomic scale using atom probe tomography (APT), which significantly enhanced our understanding of the 3D microstructure of GB complexion," said Fu.

"To investigate the effects of the GB complexion on the grain coarsening behaviors of ZrO_2 NCs, the multi-element co-doped and un-doped 65%ZrO_2-35%SiO_2 samples were annealed at different temperatures, with the un-doped samples as control group. The ZrO_2 NCs in the as-sintered sample had an average value of 40.8 nm.

"Compared with sizes of ZrO_2 NCs in the as-sintered sample, those in the 1200 ºC-annealed sample increased by 117.6%, indicating that the ZrO_2 NCs showed very strong coarsening kinetics. In comparison, compared with sizes of as-sintered ZrO_2 NCs in the multi-element co-doped sample, those in the 1200 ºC-annealed sample increased by only 19.8%, indicating that the GB complexions contributed to the strong coarsening resistance of ZrO_2 NCs," said Fu.

However, liquid phase sintering occurred in the multi-elements co-doped sample, so that the sizes of as-sintered ZrO_2 NCs in the co-doped sample were much larger than those in the un-doped sample. Future work could focus on optimizing the dopants to avoid the occurrence of liquid phase sintering.

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