Atomic-Scale Studies of Ceramic Grain Boundaries: LBNL and ORNL

Key Insights into Mechanical Properties Obtained

Unique direct atomic resolution images have been obtained that illustrate how a range of rare-earth atoms in sintering additives bond to the interface between the intergranular phase and the matrix grains in an advanced silicon nitride ceramic. It was found that each rare-earth atom bonds to the interface at a specific location, depending on atom size, electronic configuration and the presence of oxygen and that binding location can be correlated to the mechanical properties of these materials. The work is a key breakthrough in the understanding the basis for the mechanical properties in these ceramics.

Bulk silicon nitride (Si_3N_4) ceramics have been studied extensively over the last two decades. Their exceptional mechanical and physical properties, including high strength, high decomposition temperature (1900°C), and good oxidation and corrosion resistance, have made them leading candidates to operate as structural components in high-temperature applications such as gas-turbine engines functioning at temperatures exceeding the service limit (1100°C) of the presently used nickel-base superalloys. Ceramics, however, are compromised at present by an acute lack of toughness. Previous investigations have shown that improvements in the amorphous film between the grains is the key to increased toughness in these materials. As the ceramic begins to fracture and cracks grow along the boundaries, the grains become interlocked and act as a bridge across the crack wake, thereby making it more difficult for the crack to propagate. Accordingly, the intergranular film represents the key to developing tough ceramics and its chemical composition, atomic structure and bonding characteristics are critical to the material's microstructure and mechanical properties. The problem is that the intergranular films are typically only a few nanometers in thickness. Consequently, determining the local atomic structure and bonding characteristics requires characterization at Ångstrøm to sub-Ångstrøm scales. Until recently, no microscopes or chemical analysis probes were able to resolve such information at these length scales.

Recent breakthroughs in scanning transmission electron microscopy (STEM) and associated chemical analysis now permit probing of the local atom structure and bonding characteristics with a resolution close to 1 Ångstrøm. In particular, microscopists Naoya Shibata and Stephen J. Pennycook at Oak Ridge National Laboratory, in a recent *Nature* paper, demonstrated that this technique is ideal for characterization of Si_3N_4 interfaces. They imaged individual La atom sites in a nanometer-wide intergranular film and showed the La to be bonded preferentially to the grain surface. Sites observed agreed with first-principles calculations. Alexander Ziegler, working with LBNL/MSD Faculty Senior Scientist Robert O. Ritchie, used a similar instrument installed at Berkeley Lab's National Center for Electron Microscopy (NCEM) to examine a silicon nitride ceramic doped with oxides of other rare-earth elements of La, Sm, Er, Yb and Lu; these oxides are a very common sintering additives in Si_3N_4 as it has been shown empirically that their addition improves the mechanical properties. By using direct atomic-resolution imaging techniques with NCEM scientists Christian Kisielowski and Nigel D. Browning, it was possible to determine the exact location of each rare-earth atom and to see how it specifically bound to the interface between the intergranular phase and the matrix grains. Detailed analysis of the individual atomic positions of the rare-earth elements, using electron energy loss spectroscopy, also revealed the location of oxygen atoms in the atomic bonding at the interface. The choice of rare-earth elements placed in the boundary was found mechanistically to affect the macroscopic fracture toughness, thereby defining a link from sub-nanometer to meter dimensions.

This information about the specific atomic structure and bonding characteristics in advanced ceramics had been lacking for many years and should now aid the development of improved ceramics. Most importantly, these two studies will assist in understanding how ceramic microstructures evolve during fabrication; in particular how grain growth and microstructural evolution are affected by different sintering additives at the atomic level. Indeed, determination of the precise rare-earth atom location is a prime factor to understanding the origin of the mechanical properties in these ceramics and will enable precise tailoring to critically improve the materials performance in wide-ranging applications.

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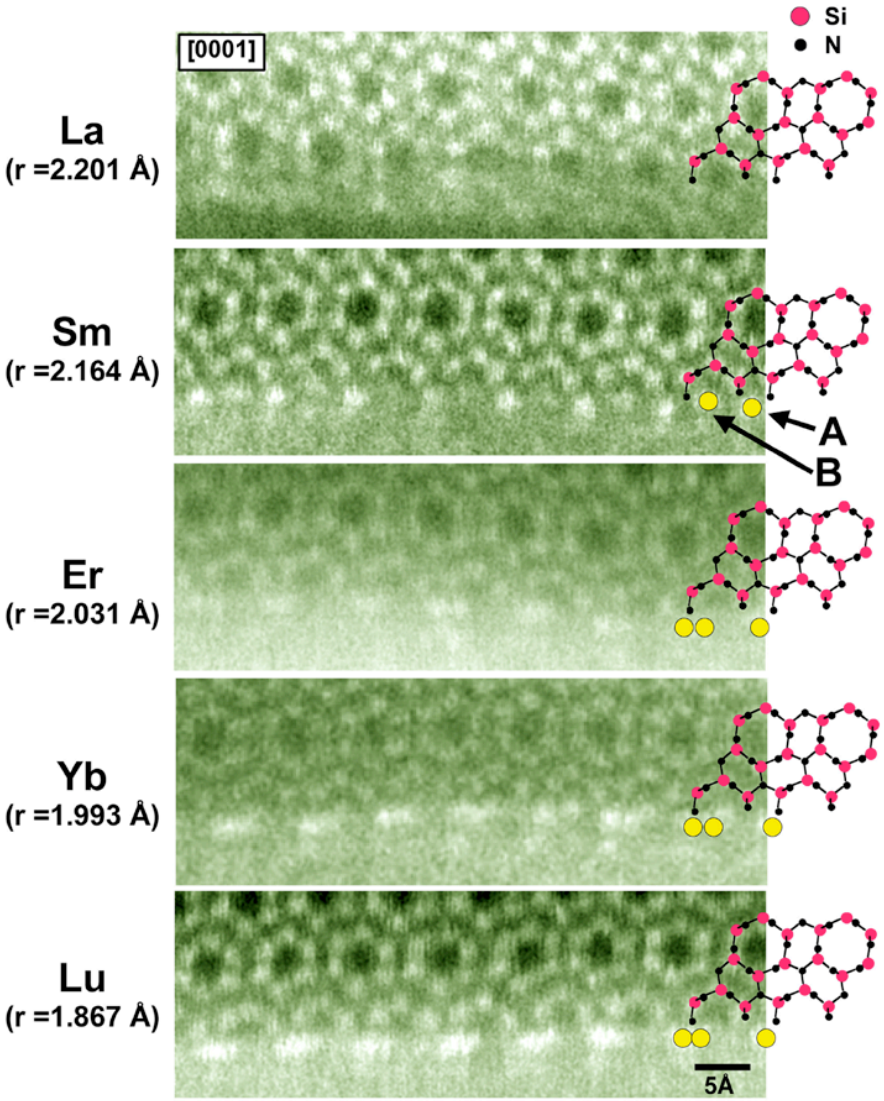

Scanning transmission electron microscopy *images of a silicon nitride (Si_3N_4) ceramic doped with a series, in decreasing order of the dopant atomic radius, of rare earth oxides (La_2O_3,Sm_2O_3, Er_2O_3, Yb_2O_3, Lu_2O_3) as sintering additives. In each image, the Si_3N_4 crystal structure abuts the intergranular phase below it with open hexagonal rings. The "Z-contrast" microscopy mode makes heavier atoms appear brighter. Two periodic sites, A, B, are highlighted along the interface and are the preferred locations of individual dopant atoms (identified as yellow dots) in the Sm doped sample. In contrast, the Er, Yb and Lu atom-pairs preferably bond to a slightly distorted A, B position, whereas no specific ordering occurs in the La doped sample. The site alterations suggest an important role of oxygen and/or ionic radius of the dopants in controlling atom attachment at the interface. Macroscopic mechanical property evaluation shows that the highest fracture toughness is achieved with the largest rare-earth ions, i.e., La, which display non-periodic/non-specific atomic attachment at the grain-boundary interface.*