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Observation of Cu-rich grain boundary nanoparticles and complexions in Cu/Ti-doped alumina

C.J. Marvel [a], M.R. Kracum [a], Z. Yu [b], M.P. Harmer [a], H.M. Chan [a,*]

[a] Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA
[b] State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, People's Republic of China

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A B S T R A C T

Alumina powders were processed with 7.8 wt% CuO and post-sintering reduction heat-treatments were applied with the aim of producing metallic grain boundary complexions. The influence of titanium co-doping was also studied. Grain boundaries were characterized by aberration-corrected scanning transmission electron microscopy. Copper grain boundary enrichment was achieved, but only in the titanium doped samples; the segregated copper exhibited a Cu^{2+} valency state, the segregated titanium exhibited Ti^{3+} or Ti^{4+} valency states, and metallic Cu nanoparticles were also observed. The crystallographic orientation of the grain boundary plane had a marked influence on concentration and oxidation state of the segregating species.

The structure and properties of grain boundaries have a critical influence on bulk material properties. Thus, the effects of additives and their segregation behavior have attracted sustained scientific interest. In the case of alumina it has been shown that reactive elements segregate strongly to grain boundaries and that elemental segregation slows diffusional transport of oxygen [1–4]. Similarly, dopant elements have been widely reported to influence grain boundary mobility and hence grain growth kinetics and microstructure development [5–9]. Recently, an increasingly popular concept termed grain boundary complexions has been invoked to describe the equilibrium state of grain boundary structures [10–14]. A grain boundary complexion can be likened to a 'phase' in terms of its thermodynamic stability and kinetic behavior, but unlike a discrete bulk phase, it cannot exist in isolation from the adjacent grains and it may possess a gradient in structure and/or composition between the adjoining grains. Researchers have identified complexions of a metallic nature in alloys [15,16], and ceramic complexions in polycrystalline ceramics [10,17,18]. In certain cases, the complexion structure consists of atomic layers of an additive element situated at the grain boundary [10,16,19].

Part of the motivation of the present study was to explore the possibility of synthesizing a metallic complexion within a ceramic material, perhaps in the form of a mono- or bilayer of metallic atoms at an alumina grain boundary. Interestingly, there has been no report of such a complexion type to date. It was deemed that a ceramic material containing metallic complexions might exhibit unique combinations of physical properties, in a manner analogous to conventional metal ceramic composites. The system would be unique, however, in the sense that the metal 'phase' would be confined to nm scale layers at the ceramic grain boundary. It was decided to initially focus on copper and alumina, since each is prototypical of its material class. A further advantage of this system is that the copper-alumina interface has been intensively studied because of the relevance to brazing and reliability in microelectronic devices.

Considering grain boundary segregation studies, to the authors' knowledge there has been no report of copper segregation in alumina. This is consistent with the body of work that has shown that high purity copper does not wet the surface of alumina [20–22]. However, wetting can be induced by the incorporation of oxygen in the copper melt [23–25]. Gonzalez and Trumble [24] showed that for molten copper infiltration of alumina compacts, a critical oxygen content of ~5 at.% was necessary. The effect of oxide additions has in turn suggested that the formation of a reaction layer of $CuAlO_2$ plays an important role in the enhanced wetting [26,27]. This is consistent with recent work of the authors that showed that $CuAlO_2$ wets alumina grains, and that under certain conditions it can be reduced to a novel copper-alumina hierarchical microstructure [28–30]. The purpose of the current study, therefore, was to explore whether a continuous metallic copper complexion could be achieved by first infiltrating alumina grain boundaries with the $CuAlO_2$ phase, then heat-treating under reducing conditions to convert the $CuAlO_2$ to copper and alumina. Additionally, the influence of Ti additions was investigated, as several studies have shown that

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* Corresponding author.
E-mail address: hmc0@lehigh.edu (H.M. Chan).

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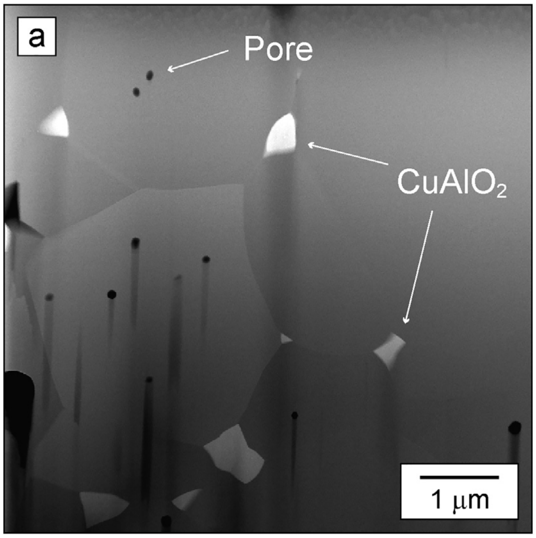

Fig. 1. HAADF image showing α-Al_2O_3 grains, porosity, and $CuAlO_2$ second phases in the reduced Cu/Ti co-doped specimen. Notably the $CuAlO_2$ phases exhibited a wetting morphology.

alloying copper with titanium greatly enhances the wetting of alumina [20,31–34].

Starting powders with the overall composition Al_2O_3–7.8 wt% CuO were produced by mixing α-Al_2O_3 (99.999% Sumitomo) and CuO (99.9995% Fisher Scientific) powders in the appropriate ratio. This CuO content corresponds to ~5 vol% metallic copper on complete reduction and was chosen based on preliminary results that showed it was consistent with a fine, uniform dispersion of copper second phase situated at the alumina triple points. The powders were subsequently milled with alumina milling media (99.8%, 3 mm diameter, Union Process) in 200 proof ethanol. For the Ti-doped samples, a solution of titanium (IV) isopropoxide (99.995% Fisher scientific) was added to the Al_2O_3-CuO powder mixture during the milling process. The dopant level of Ti was 1000 ppm (Ti/Al cation ratio). The powders were subsequently dried and isostatically pressed into disk-shaped pellets (40 ksi for 25 min). Densification was carried out using field assisted sintering (Thermal Technologies LLC, SPS-10-3) at 1300 °C for 25 min at 50 MPa pressure. To convert the Cu-rich phases to $CuAlO_2$, the samples were packed in alumina powder and annealed in air at 1100 °C for 48 h using a box furnace (Rapid Temp CM Inc.). Reduction treatments were conducted using a vacuum furnace (M60, Centorr Vacuum Industries) in a 5% H_2 – N_2 reducing atmosphere at 1000 °C for 3 h.

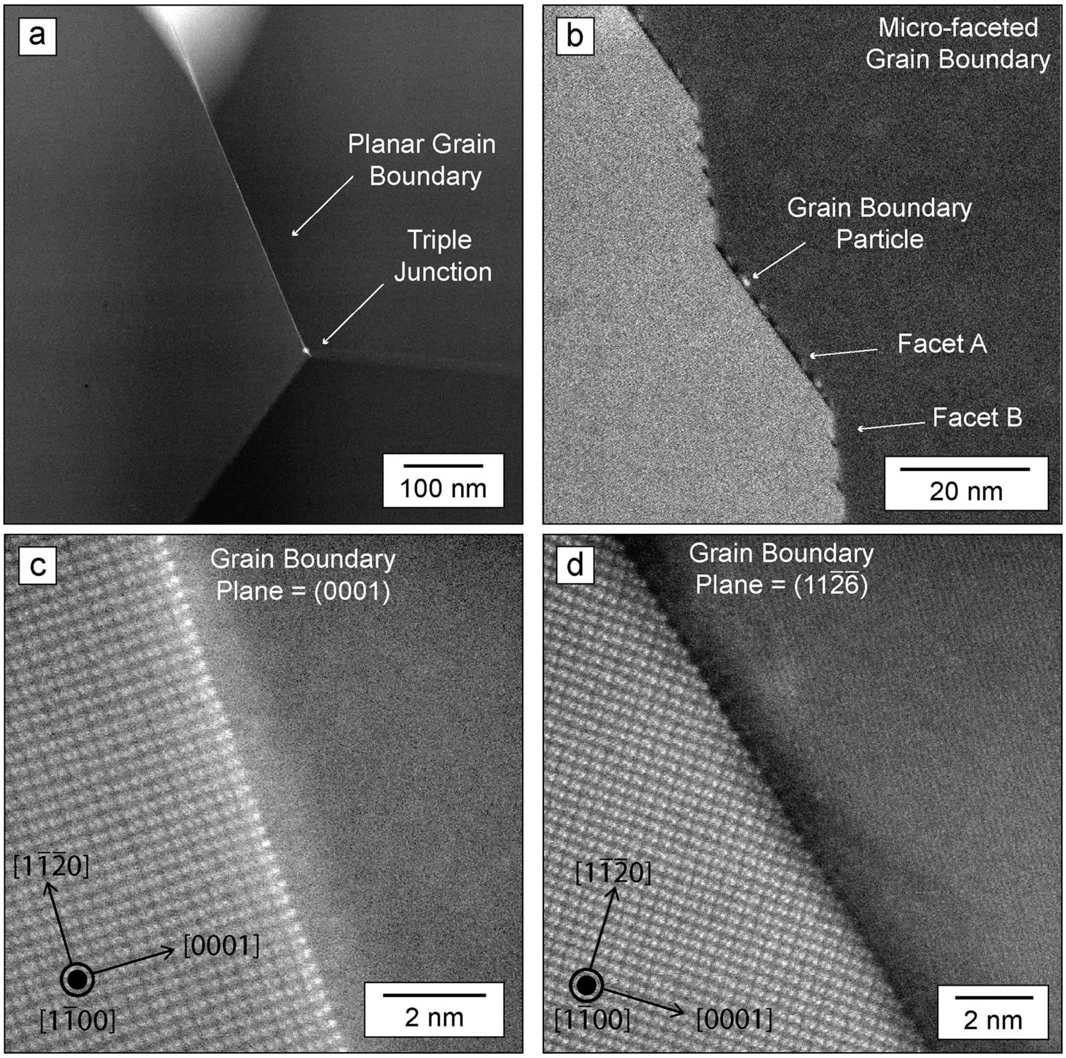

Fig. 2. HAADF images showing two grain boundary types observed in the reduced Cu/Ti co-doped specimen: (a) an ordered complexion type exhibiting segregation of heavy atomic species and (b) a micro-faceted grain boundary that exhibited grain boundary particulates. Parts (c) and (d) are higher magnification images taken from the planar boundary and facet A labeled in parts (a) and (b), respectively. The high intensity observed on the planar boundary and particulate phases indicates that species heavier than the matrix Al and O ions are preferentially segregated to the grain boundaries, and in the case of the dark intensity of facet A or B, there is evidence of lighter elements segregating to the boundaries.