

## Structural Features of Y and Zr Segregated Grain Boundaries in Alumina from EXAFS Measurements

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Abstract No. Wang1489

Beamline(s): X23A2

**Introduction:** Dopants Y and Zr at the level of 100 to 1000 ppm have been found to enhance alumina creep resistance at high temperatures by two orders of magnitude.<sup>1, 2</sup> We have used EXAFS<sup>3, 4</sup> to investigate grain boundary segregation of Y in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and evolution of the structural environment around the Y atoms. The dopant segregation in these samples had also been characterized by high resolution scanning transmission electron microscopy.

**Methods and Materials:** The materials were ultra high purity  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> doped with Y<sub>2</sub>O<sub>3</sub> at two levels, 100 ppm and 1000 ppm (Y/Al atomic ratio, and the specimens are referred as 100Y and 1000Y). Annealing at 1475°C for times ranging from 15 to 50 h was used to obtain samples with different grain sizes, and therefore different amounts of dopant grain boundary segregation. Y-coated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles were prepared by sol-gel processing using Boehmite sol and Y-acetylacetonate precursors. Y K-edge EXAFS measurements were made with fluorescence detection. Transmission absorption measurements were made for Y<sub>2</sub>O<sub>3</sub> powder and fluorescence measurements were made for polycrystalline YAG as standards.

**Results:** Parameters obtained by fitting EXAFS spectra are shown below for different grain boundary concentrations and for Y on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particle surface:

Fitting results for the Y-O shell

	Y concentration	R (Å):	N	$\sigma^2(\text{Å}^2)$ :
Grain Boundary	Dilute (I)	2.30 ± 0.01	4.2 ± 0.5	0.009 ± 0.001
	Super. Sat. (II)	2.30 ± 0.01	5.0 ± 0.5	0.01 ± 0.001
	Equi. YAG (III)	2.36 ± 0.01	7.5 ± 0.7	0.008 ± 0.0008
Particle	Surface	2.33 ± 0.01	4.8 ± 0.5	0.008 ± 0.0005

Fitting results for the Y-Al shell

	Y concentration	R (Å):	N	$\sigma^2(\text{Å}^2)$ :
Grain Boundary	Super. Sat. (II)	3.31 ± 0.01	1.3 ± 0.5	0.001 ± 0.0005
Particle	Surface	3.31 ± 0.01	1.2 ± 0.5	0.002 ± 0.0005

**Conclusions:** The incorporation of Y atoms by  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> grain boundaries, on average, is characterized by three composition regimes: (I) dilute to saturated; (II) supersaturated. The average Y grain boundary concentration in equilibrium with YAG precipitates has been determined to be  $\sim 1/4$  equivalent monolayer, and the maximum supersaturation concentration has been determined to be  $\sim 1/2$  equivalent monolayer. EXAFS reveals that accompanying the supersaturation of grain boundaries with Y is an increasing Y-O nearest neighbor coordination number and, simultaneously, a significantly increased degree of ordering of Y with respect to Al ions beyond nearest neighbor O. This Y-Al distance is the same as that for Y absorbed on the free surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and the same as that expected for the Y-Al distance when Y substitutes for Al with the Y-O distance relaxed to that in Y<sub>2</sub>O<sub>3</sub>. This compositional and structural information has led to a clear picture on how the grain boundary segregated Y concentration influences grain boundary structure. For dilute Y concentrations, Y ions preferentially fill sites in the grain boundary core which have well defined order only within the nearest neighbor shell of oxygens. As the Y concentration increases, Y begins to occupy near-boundary sites, forming two near-boundary layers each is adjacent to a grain surface. The near-boundary layer has nearest neighbor ordering extending at least to nearest neighbor cations. Nucleation of the YAG phase leads to the depletion of Y from these two partially ordered layers.

**Acknowledgments:** The authors thank Dr. Joseph Woicik and Dr. Zugen Fu for assistance in beamline operation and data acquisition, and for beneficial discussions. This research is supported by the U.S. Air Force Office of Scientific Research under Contract No. F49620-98-1-0117 (monitored by Dr. A. Pechenik) and by the U.S. Office of Naval Research under Contract No. N00014-99-1-0236 (monitored by Dr. S. Fishman).

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