

Corrosion behavior of Al₂O₃ in static state water vapor environment at high temperature

S. UENO, D. D. JAYASEELAN, N. KONDO, T. OHJI, S. KANZAKI
 Synergy Materials Research Center, National Institute of Advanced Industrial Science and Technology,
 2268-1 Shimo-Shidami, Moriyama-ku, Nagoya 463-8687, Japan
 E-mail: shunkichi.ueno@aist.go.jp

Water vapor corrosion test at 1500 °C for single crystal and polycrystalline Al₂O₃ was performed in static state water vapor environment. In both cases, there was an increase in weight. The lattice parameter for polycrystalline bulk decreased by the corrosion test. The grain surface was corroded by water vapor and terrace fields were generated. No anisotropic corrosion behavior was observed.

Alumina is a hopeful material for high temperature application due to its high stability at elevated temperatures [1]. Because the oxygen diffusion in alumina at high temperatures is low enough [2], it is considered that alumina phase is a promising material for oxidation protection layer for metal or non-oxide ceramics in high temperature applications.

Non-oxide ceramics, such as silicon nitride and silicon carbide, oxidize at high temperatures and form a silica layer on their surface. It is known that the silica phase easily corrodes in water vapor environment at high temperatures [3, 4].

Recently, Yuri and Hisamatsu reported the recession rate for pure Al₂O₃ at high temperature and high water vapor partial pressure in high velocity gas flow [5]. In that report, the recession rate of Al₂O₃ is high enough when compared to that of silicon nitride, i.e., Al₂O₃ is easily corroded in actual gas turbine environment.

A detailed recession rate expression for polycrystalline Al₂O₃ in actual combustion gas flow was derived previously [5]. However, Yue *et al.* reported that no weight change was observed by the water vapor corrosion test in static state water vapor environment at 1700–2000 °C [6]. On the other hand, Tai *et al.* suggested that the weight of Al₂O₃ phase increased in water vapor environment at high temperatures, even if the boundary phase was corroded and removed [7]. In that report, the weight is decreased up to 1500 °C and is increased above 1600 °C in Ar-H₂O static state environment [7]. More detailed consideration of water vapor corrosion mechanism has not been established yet.

Al₂O₃ (99.99% purity, High Purity Chemicals Co. Ltd.) powder was used as the starting material for preparing single crystalline and polycrystalline Al₂O₃. The high temperature water vapor corrosion test was performed for single crystal and polycrystalline Al₂O₃ using a Corrosion Testing Machine (Japan Ultra-high Temperature Materials Research Center). The sample was placed on a high purity Al₂O₃ plate and then heated under the following conditions; temperature: 1500 °C,

time: 100 hrs, gas flow: 30 wt% water (air:H₂O = 70:30 (wt %)), gas flow rate: 175 ml/min that correspond to gas velocity 4.6×10^{-4} m/s. To exclude the water vapor corrosion occurring at low temperatures, the corrosive gas was introduced when the temperature reached 1500 °C and the gas flow was stopped after the 100 hrs testing period.

The density of the sintered polycrystalline Al₂O₃ bulk was 3.581 g/cm³ that is 90.0% of ideal value. No remarkable changes in external view for polycrystalline bulk were observed after the corrosion test.

The weights of the samples (single crystalline and polycrystalline Al₂O₃) were increased during the corrosion test. The weight gain for single crystal and

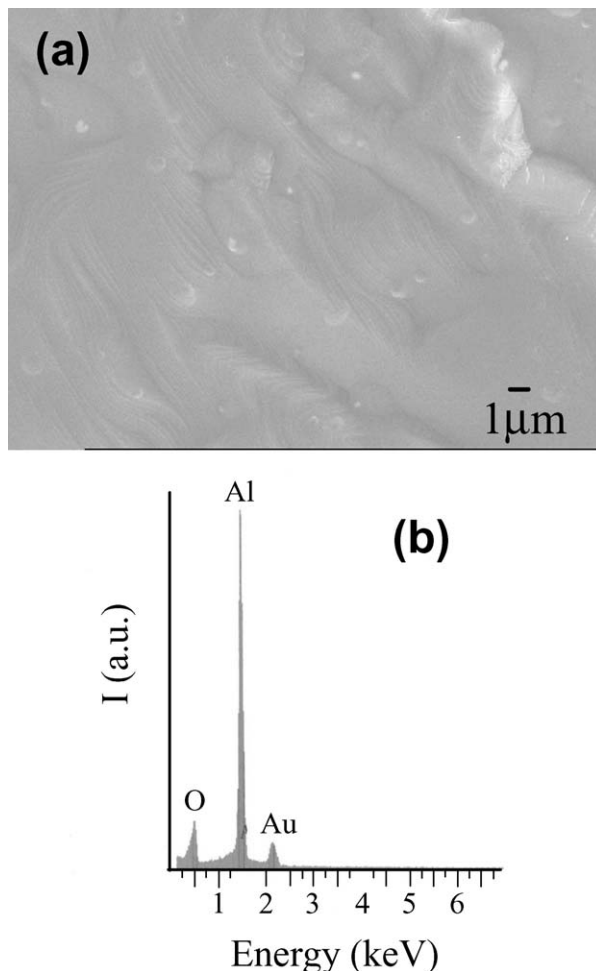


Figure 1 The surface of the single crystalline Al₂O₃ after the corrosion test sample (a) and corresponding EDX analysis (b).

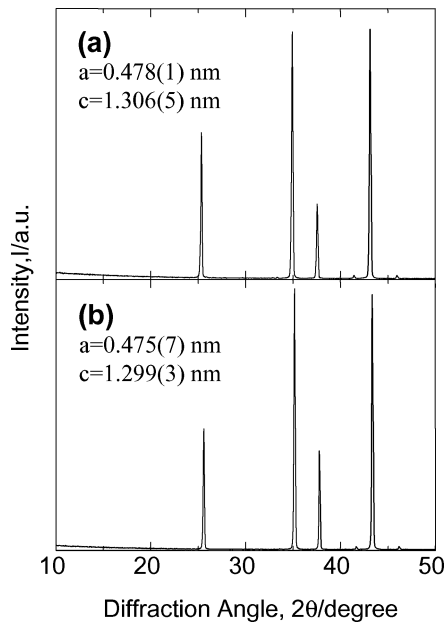


Figure 2 X-ray diffraction patterns for polycrystalline bulk (a) before and (b) after the corrosion test.

polycrystalline bulk were 2.5×10^{-6} g/cm²·hr and 1.7×10^{-6} g/cm²·hr for 100 hrs test, respectively. Because the water vapor flow was stopped after the 100 hrs testing period and cooled down to room temperature in dry air, it is considered that the formation of hydroxyl group on the grain surface was avoided in the cooling step. In this study no evidence for the existing hydroxyl group on the polycrystalline bulk and single crystal sample surface could be observed by IR spectroscopy analysis. The weight was slightly increased in both cases. To confirm the existence of impurity element at sample surface, energy dispersive X-ray (EDX) analysis was carried out on the single crystalline Al₂O₃ after the corrosion test. The analysis was performed in the area indicated by Fig. 1a. No impurity element was observed as shown in Fig. 1b, where coated Au was observed. Tai *et al.* suggested the partial pressure of Al(OH)₃ and/or Al(OH)₂ vapor species at 1500 °C is about 10⁻⁵ kPa in 24.7 kPa water vapor partial pressure [7], where total pressure is 100 kPa. Yuri and Hisamatsu suggested that the recession rate of Al₂O₃ in high velocity

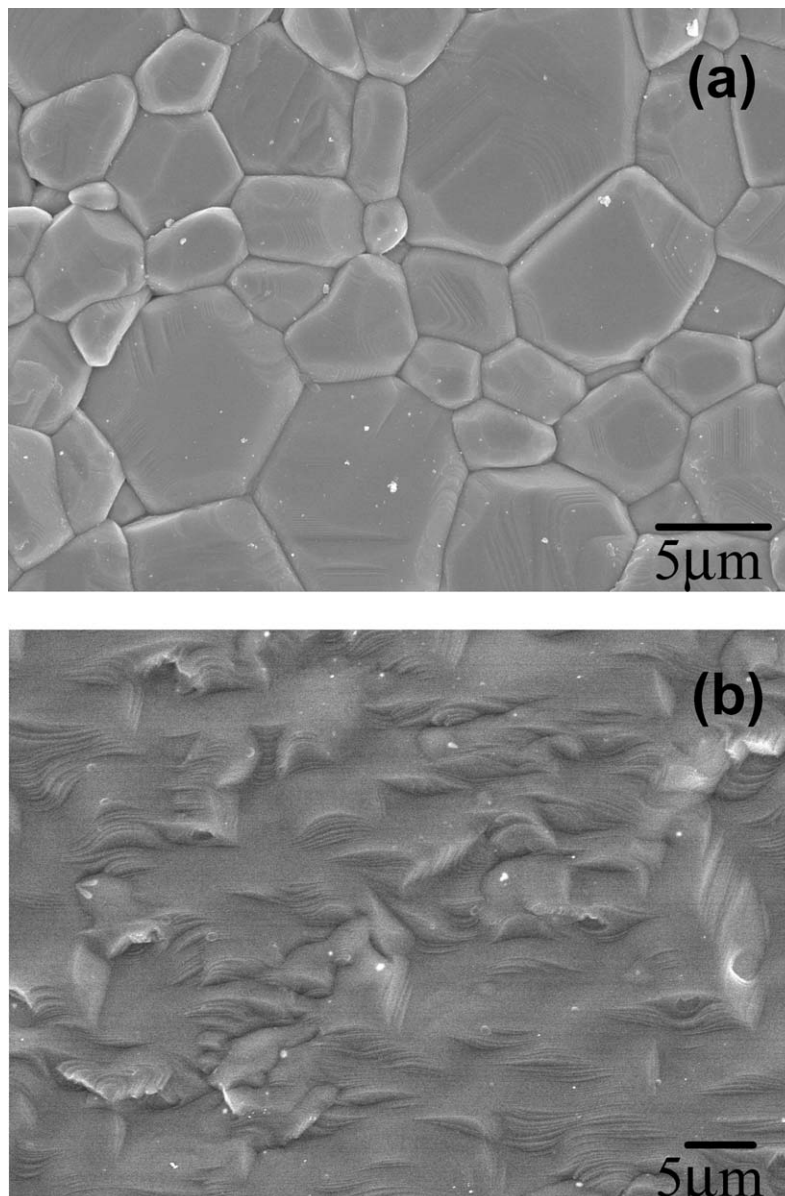


Figure 3 SEM images of after corrosion test: (a) polycrystalline bulk sample surface and (b) single crystal surface.

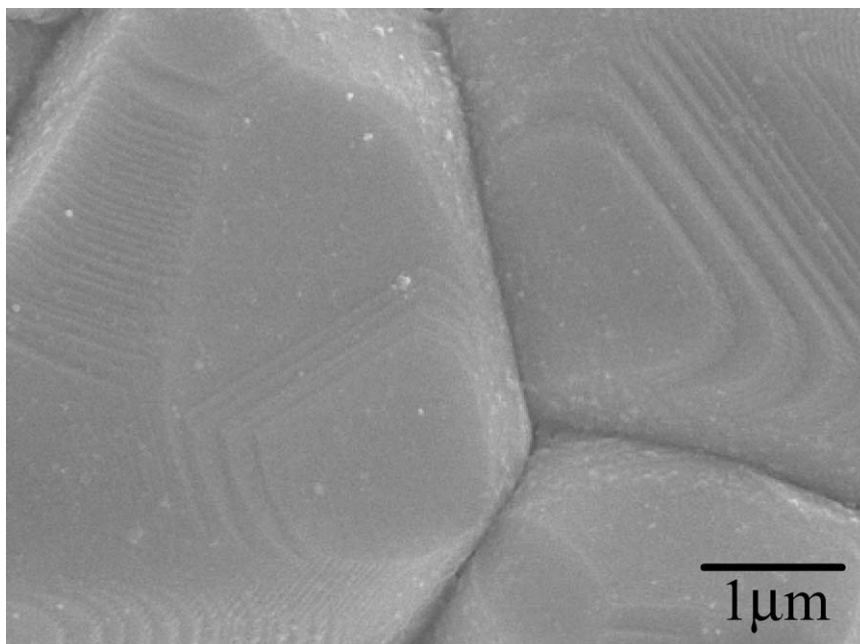


Figure 4 Enlarged image of Fig. 2a.

combustion gas flow at 1500 °C estimated $k_w = 3.81 \times 10^{-1} \cdot \exp(-246 \text{ (kJ/mol)/RT}) \cdot p_w^{1.51} \cdot Re^{0.8} / P$, where p_w , Re and P denote water vapor partial pressure, Reynolds number and total pressure [5]. The above references suggested that Al_2O_3 react with water vapor and volatilize as Al-O-H species. However, in our experiment the weight of the sample was slightly increased at 1500 °C in static state water vapor environment. Tai *et al.* also reported that the weight of Al_2O_3 is slightly increased above 1600 °C in static state water vapor environment [7].

Fig. 2a and b show the X-ray diffraction patterns for polycrystalline bulk before and after the corrosion test, respectively. All peaks could be indexed as corundum phase. No phase changes were observed during the test. The relative intensity for each peak was also unchanged by the corrosion test. The lattice parameters for these samples were calculated by mean square method. The lattice parameters for before testing sample were $a = 0.478(1)$ nm and $c = 1.306(5)$ nm and for after testing sample were $a = 0.475(7)$ nm and $c = 1.299(3)$ nm, respectively. The lattice parameters decreased slightly by the corrosion test.

Fig. 3a and b show Scanning Electron Microscopic (SEM) images of after corrosion test polycrystalline bulk sample surface and single crystal surface, respectively. A peculiar pattern similar to sand ripples or terrace fields could be observed in both cases. Fig. 4 shows enlarged image of Fig. 3a. Apparently, it is recognized that the water vapor corrosion of Al_2O_3 grain surface occurs anisotropically in some direction. In the case of water vapor corrosion of Al_2TiO_5 phase, terrace fields

similar to Fig. 3 were generated by anisotropic water vapor corrosion [8]. In that case, relative intensities of some particular peaks were changed during the corrosion test [8]. However, in this experiment, the relative intensity of all the peaks were unchanged during the corrosion test as shown in Fig. 2. By the water vapor corrosion, the weight of Al_2O_3 bulk must be reduced. One possible model for the weight gain in this experiment could be considered as the result of the combination of the weight gain by water vapor diffusion into Al_2O_3 lattice and the weight loss by the water vapor corrosion of Al_2O_3 grain surface.

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