Anisotropic Behavior of Water Vapor Corrosion of Rutile TiO₂ at High Temperature*

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Water vapor corrosion behavior of rutile TiO₂ was examined at 1773 K in 30 mass% H₂O environment. The corrosion rate for this sample was 2.2×10^{-4} kg·m⁻²·h under this experimental conditions. Anisotropic corrosion behavior was recognized in the planes that are parallel to *c*-axis. Many rectangular shaped etch-pits were generated at the grain surfaces. The corrosion proceeded from the side wall of the etch-pits and then, terrace fields were grown on the grain surface. Ridge-shaped microstructure was observed on the side wall of the terrace owing to the anisotropic corrosion.

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1. Introduction

To clarify the stability of minerals in mantle, the solubility of minerals into hot water has been examined at high temperatures and pressures.¹⁻³⁾ The solubility of rutile TiO₂ in hot water at high temperatures is smaller enough than those of other minerals, such as, SiO₂, Al₂O₃, etc.^{1,2)} It was reported that TiO₂ is soluble appreciably into H₂O, especially at high temperature and under low pressure to form neutral species of Ti(OH)₄.¹⁾

Because the band gap energy of TiO₂ is fairly large up to about 3.05 eV, it is known that TiO₂ is highly stable against photocorrosion in water.⁴⁾ However, Harris and Wilson suggested that reduced TiO₂ which was used as an anode in a photoelectrochemical cell corroded in an aqueous solution of H₂SO₄.^{5,6)} In this case, anisotropic corrosion occurred in the photoelectrochemical reaction process.⁵⁾ The corrosion was considered to have a close relation to hole concentration as follows,⁴⁾

Because the solubility of TiO₂ in hot water is small, TiO₂ and/or its complex oxides are hopeful materials for barrier application against their environment, especially, in water vapor environment at high temperatures. However, detailed corrosion mechanism in hot water and/or water vapor at high temperatures has not been examined yet.

In this study, the water vapor corrosion test for rutile TiO₂ was examined at 1773 K and the corrosion mechanism was discussed.

2. Experimental Procedure

TiO₂ (rutile) powder (99.99% purity, High Purity Chemicals Co., Ltd.) was used as the starting material. TiO₂ powder was pressed into pellet and then, annealed at 1873 K in air for 12 h. Then, the sample was slowly cooled down to the room temperature.

High temperature water vapor corrosion test was per-

formed using the Corrosion Testing Machine (Japan Ultra-high Temperature Materials Research Center). The sample was kept on a TiO₂ jig. The corrosion test conditions were as follows; Temperature: 1773 K, Time: 100 h, Flow gas: 30 mass% water (air:H₂O = 70:30 (mass%)). The corrosive gas was introduced into the furnace when the temperature reached 1773 K and it was stopped after the testing period of 100 h.

The surface structures were observed by scanning electron microscope (SEM) and the phase was identified by X-ray diffraction method.

3. Results and Discussion

The actual density of the pellet was 3695 kg·m⁻³, that is 87% of the theoretical value. The weight decreased during the corrosion test and the corrosion rate was calculated as 2.2×10^{-4} kg·m⁻²·h for this experimental conditions.

Figure 1 shows X-ray diffraction patterns of the sample surface (a) before and (b) after corrosion test, respectively. The X-ray diffraction pattern of (a) can be identified as rutile structure with no impurity phase. The relative intensities for all peaks excepted 110 peak decreased during the corrosion test. Especially, relative intensity of 200 peak decreased drastically. These results suggest that the corrosion occurred anisotropically in the crystal planes those are parallel to *c*-axis.

Figures 2(a) and (b) show the typical microstructures that were formed by the corrosion. In many places, terraced fields are observed on the surface of individual grains as shown in Fig. 2(a). On the other hand, in some places, deep etch-pits are observed as shown in Fig. 2(b). The etch-pits resemble exactly rectangle shape and the depth of the etch-pits are more than 10 μm. Because the grain surface that shows etch-pits as shown in Fig. 2(b) do not show terrace field, it is considered that such grains escaped from intense corrosion during the test.

Figures 3(a) and (b) show the enlarged landing of the terrace field and the edge of the etch-pit, respectively. The landing of the terrace field is rectangle in shape, as the etch pits shown in Fig. 2(b). At the edge of the etch pit in Fig. 3(b), it is seen clearly that the terrace is beginning to form.

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Fig. 1 X-ray diffraction patterns of bulk surface rutile TiO_2 ; (a) before and (b) after corrosion test, respectively.

Fig. 3 The enlarged images of (a) the landing of the terrace fields and (b) edge of the etch-pit, respectively.

Fig. 2 The typical microstructures that were formed by the corrosion; (a) terraced fields structure and (b) deep etch-pits.

From these results, the water vapor corrosion mechanism for TiO_2 could be considered as the illustrations shown in Figs. 4(a) and (b). First, rectangle-shaped etch-pits are generated toward one crystal direction as shown in Fig. 2(b). On the edge of the etch-pit near grain surface, perpendicular corrosion to the etch-pit begins as shown in Fig. 3(b). And then, the terrace fields as shown in Fig. 2(a) are generated. Because the etch-pit corrosion had a limit in depth and the terrace fields formed dominant microstructure on the corroded grain surface, namely, TiO_2 was severely corroded in the direction which was perpendicular to the etch-pits corrosion direction, it is considered that the crystal plane of the terrace has the highest corrosion resistance and the corrosion resistance of the plane which are perpendicular to the terrace is low. The reason for the generation of etch-pits could not be found in this experiment. The shape of etch-pits was very similar to that cited previously.⁵⁾ That is, the anisotropic corrosion in photoelectrochemical cell occurs on the crystal plane that are parallel to c -axis.⁵⁾ In this experiment, an anisotropic corrosion occurred on the crystal plane that are parallel to c -axis. Therefore, the nature of the corrosion in this case would be similar to that suggested by Harris *et al.*⁵⁾ So it can be assumed that some reduced phase

Fig. 4 Scheme of corrosion mechanism for rutile TiO₂; (a) formation of etch-pits at an early stage and (b) formation of terrace fields.

was generated on the grain surface of TiO₂ and then, the etch-pit was generated with the reaction concerning a hole as well as the Ref. 5.

The bottom landing of terrace field had regularly rectangle shape as shown in Fig. 3(a). However, the side wall of upper field was not straight in large scale. Figure 5 shows the enlarged image of the terrace side wall. The side wall was not a flat plane. It was observed that the ridge-shaped microstructure consisted of two equivalent crystal planes. Because TiO₂ has tetragonal lattice structure, in the case of the anisotropic corrosion in photoelectrochemical cell, TiO₂ forms nano-honeycomb structured corrosion front whose wall consists of {100} crystal plane.⁴⁾

On the other hand, solubility of TiO₂ in hot water is considered to proceed in the following reaction to form neutral Ti(OH)₄.¹⁾

It was reported that some striations were formed on the surface of rutile TiO₂ during the hot water corrosion.¹⁾ However, the surface microstructure that generated by anisotropic corrosion in this study is not similar to that of the Ref. 1.

From above discussion, the nature of corrosion behavior in this study is similar to that of photoelectrochemical corro-

Fig. 5 Enlarged SEM image of side wall of the terrace fields.

sion. Consequently, it is considered that the anisotropic corrosion in this case has a close relation to the reducing reaction of TiO₂ on the surface.

4. Conclusions

Rutile TiO₂ was corroded anisotropically in water vapor at high temperature. The corrosion behavior was similar to that of photoelectrochemical corrosion. Anisotropic corrosion occurred on the planes that were parallel to the c-axis. Rectangle etch-pits were generated first, then, terrace fields were formed. The side wall of the terrace consisted of two equivalent crystal planes.

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