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Kirkendall-like Voids Produced by Surface Diffusion

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Solid-state reactions in ceramic materials have been investigated for many years under both fundamental and technological points of view. Recently, we have investigated thin film solid state reactions of BaO vapour with (110) and (100) TiO_2 (rutile) surfaces forming variuos Ba-Ti-O phases [1,2,3]. Large holes had been occasionally observed during those investigations at the interface with the rutile substrate at 900°C [1,3]. However, the mechanism of pore formation was not considered in detail. Consequently, the aim of the present work is to study the mechanism of void formation during vapour-solid reaction between BaO vapour and (100) TiO_2 surfaces at 900°C.

The vapour-solid reactions between BaO vapor and (100) TiO_2 substrates were performed in a high-vacuum chamber as described in [3,4]. Microstructure analysis of the interfaces between the thin films and the substrates was performed by cross sectional transmission electron microscopy (TEM). TEM investigations were carried out in a Philips CM 20 T (at 200 keV) whereas a JEOL 4010 was applied for high-resolution TEM (HRTEM).

Fig. 1 shows a typical HRTEM image of Ba-Ti-O islands formed after vapour-solid reaction of a BaO quantity equivalent to a nominal film thickness of 1 nm with the (100) TiO_2 surface at 900°C. The $B_6Ti_{17}O_{40}$ Ti-rich phase was identified by a Fast Fourier Transformation of the corresponding HRTEM image (Fig. 1(b)). Similar grains were observed in other parts of the TEM sample. Increasing the nominal thickness of BaO up to 5 nm, the average size of Ti-rich grains increased as shown in Fig. 2(a). In addition, cavities between the Ti-rich grains were formed (Fig. 2(b)). After vapour-solid reaction with a BaO quantity equivalent to a nominal film thickness of 50 nm [2] or 100 nm [1], a thin film consisting of $B_6Ti_{17}O_{40}$ and $BaTiO_3$ grains was formed. In addition, large pores were developed during the reaction, at the interface with the (100) TiO_2 substrate [1].

Based on TEM investigations, the following mechanism of pore formation on (100) TiO_2 surfaces at 900°C can be considered. After vapour-solid reaction with a BaO quantity equivalent to a nominal film thickness of 1 nm the formation of $B_6Ti_{17}O_{40}$ islands was observed. No voids are formed at the TiO_2 (rutile)/Ti-rich interface at this stage of the reaction as shown in Fig. 3(a). The Ti-rich phase nucleates by Ba in-diffusion while the film growth proceeds mainly by surface diffusion [3]. Thus, with increasing reaction time (amount of BaO), cavities are formed between neighbouring islands as shown in Fig. 3(b). Since surface diffusion of TiO_2 species along the TiO_2 surface is relatively easy and fast, the cavities are produced by out-diffusion of the TiO_2. Further reaction leads to the coalescence of the Ti-rich islands over the cavities as shown in Fig. 3(c). Consequently, voids are formed. The formation of voids during interface diffusion is a well-known phenomenon in metallic systems. This effect is usually attributed to the Kirkendall effect [4]. The latter was originally observed in bulk diffusion couples of Cu and CuZn (alpha-brass or Cu-30wt% Zn). We conclude that in our case the pores are produced mainly by surface diffusion of TiO_2.

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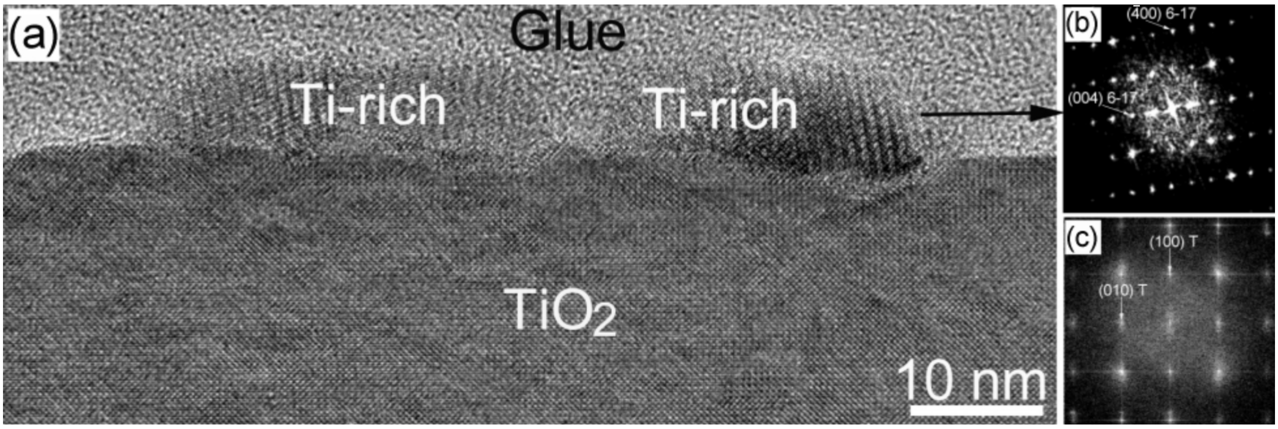

Fig. 1. HRTEM image of a sample after the reaction of a BaO vapour with a (100) TiO_2 substrate at 900°C. The nominal thickness of BaO was 1 nm. (a) Ti-rich islands on the rutile substrate. (b) and (c) FFT images of a $Ba_6Ti_{17}O_{40}$ (6-17) grain and the rutile (T), respectively. Viewing direction is [010] $Ba_6Ti_{17}O_{40}$ || [001] TiO_2.

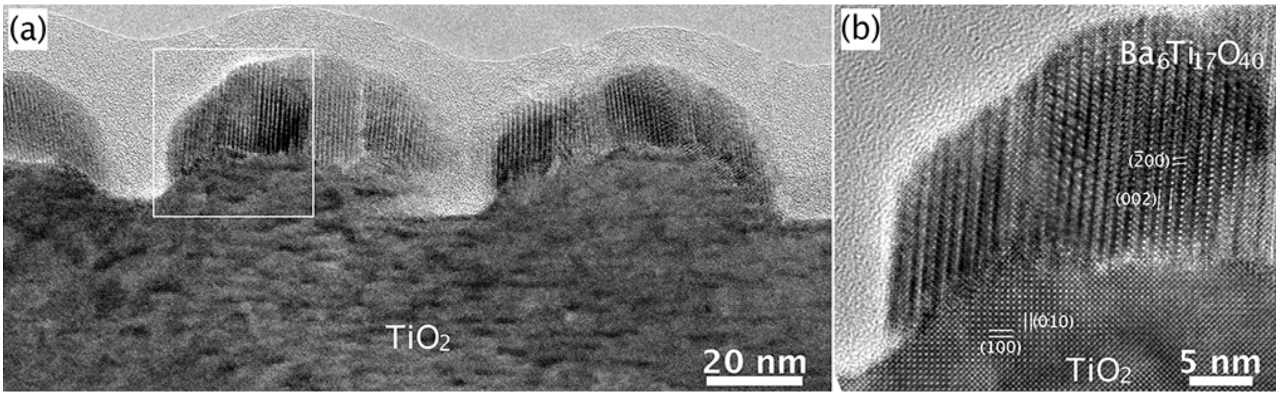

Fig. 2. HRTEM images of a sample after the reaction of a BaO vapour with a (100) TiO_2 substrate at 900°C. The nominal thickness of BaO was 5 nm. (a) Overview. (b) lattice plane images of a $Ba_6Ti_{17}O_{40}$ grain and the rutile substrate. Viewing direction is [010] $Ba_6Ti_{17}O_{40}$ || [001] TiO_2.

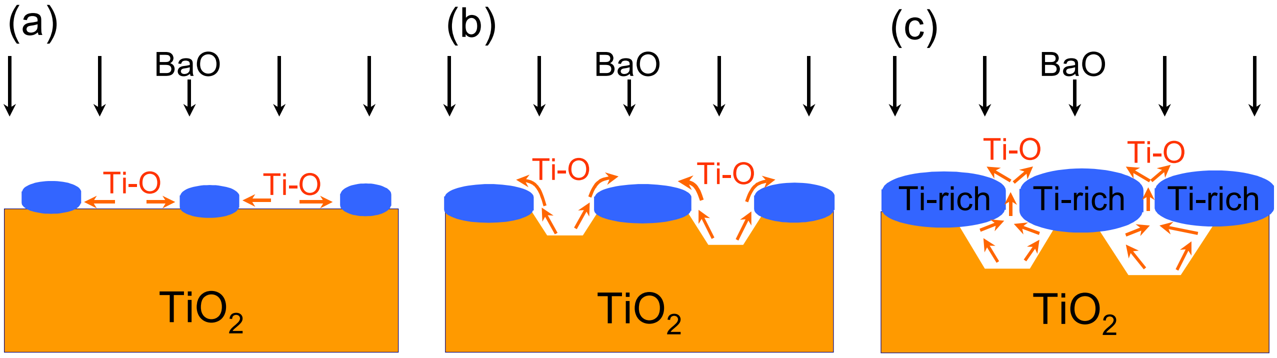

Fig. 3. Schematic diagram of void formation.