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**MICROSTRUCTURAL CHARACTERIZATION OF THE REACTION PRODUCT REGION FORMED DUE TO THE HIGH TEMPERATURE INTERACTION OF ZnO[0001] SINGLE CRYSTAL WITH LIQUID ALUMINIUM**

**CHARAKTERYSTYKA MIKROSTRUKTURALNA STREFY PRODUKTÓW REAKCJI UTWORZONYCH W WYNIKU WYSOKOTEMPERATUROWEGO ODDZIAŁYWANIA MONOKRYSTALICZNEGO ZnO[0001] Z CIEKŁYM ALUMINIUM**

The study was focused on the microstructure characterization at the micro- and nano scale of the reaction product region (RPR) formed due to the interaction between the liquid aluminum and ZnO<sup>SC</sup>[0001] single crystalline substrate at 1000°C. The research was carried out on the Al/ZnO couple produced by the sessile drop method under vacuum within two different procedures: 1) classical contact heating and cooling; 2) pushing drop procedure allowing opening the Al/ZnO interface at the test temperature and, therefore, prevent influence of cooling with Al drop on interface structure. The microstructure observations of the sample after using classical contact heating procedure revealed the formation of the RPR of ~50 μm in thickness extending into the ZnO<sup>SC</sup> single crystal substrate. It was composed of the ceramic α-Al<sub>2</sub>O<sub>3</sub> and metallic Al(Zn) mutually interpenetrating lattices, typical for the C<sup>4</sup> type structure. Additionally, at the ZnO/RPR interface, the presence of a thin (~250 nm) layer of the metastable δ-Al<sub>2</sub>O<sub>3</sub> was detected. The obtained results were compared with experimental data found for the sample after pushing drop procedure resulting in the formation of two layers of ZnAl<sub>2</sub>O<sub>4</sub> spinel and alumina, exhibiting strong epitaxial growth. The selected area diffraction patterns clearly evidenced that the crystal structure of formed Al<sub>2</sub>O<sub>3</sub> corresponds to the tetragonal δ-phase.

*Keywords:* Al/ZnO interface, in situ composites, redox reaction, α-Al<sub>2</sub>O<sub>3</sub>, δ-Al<sub>2</sub>O<sub>3</sub>, γ-Al<sub>2</sub>O<sub>3</sub>

W pracy scharakteryzowano mikrostrukturę w skali mikro i nano strefy produktów reakcji (SPR) powstałych w wyniku oddziaływania pomiędzy ciekłym aluminium i monokrystalicznym podłożem ZnO<sup>SC</sup> o orientacji [0001] w 1000°C. Badania przeprowadzono dla pary Al/ZnO wytworzonej w próżni metodą kropli leżącej przy zastosowaniu dwóch procedur: 1) klasycznej, wspólnego nagrzewania i chłodzenia, 2) przepychania kropli, umożliwiającej otwarcie granicy rozdziału Al/ZnO w temperaturze badania, a tym samym uniknięcia wpływu chłodzenia kropli Al na jej strukturę. Obserwacje mikrostruktury próbki po zastosowaniu klasycznej procedury wspólnego wygrzewania wykazały powstanie SPR o grubości około 50 μm wewnątrz podłoża ZnO. Składała się ona z dwóch wzajemnie przenikających się sieci ceramicznej α-Al<sub>2</sub>O<sub>3</sub> i metalicznej Al (Zn), typowych dla struktury C<sup>4</sup>. Dodatkowo, na granicy ZnO/RPR wykryto obecność cienkiej (~250 nm) warstwy metastabilnej odmiany δ-Al<sub>2</sub>O<sub>3</sub>. Uzyskane wyniki porównano z danymi doświadczalnymi znalezionymi dla próbki po procedurze przepychania kropli, która skutkowała w tworzeniu się dwóch warstw wykazujących silnie epitaksjalny wzrost: spinelu ZnAl<sub>2</sub>O<sub>4</sub> oraz tlenku aluminium. Dyfrakcje elektronowe pokazały, że struktura krystaliczna utworzonej Al<sub>2</sub>O<sub>3</sub> odpowiada tetragonalnej fazie delta.

**1. Introduction**

Research interest has recently been directed towards the *in situ* metal-ceramic composites, in which reinforcing phase forms during processing due to chemical reactions. A wide family of Al-Al<sub>2</sub>O<sub>3</sub> composites can be made by *in situ* synthesis using the redox reactions between liquid aluminum and binary or complex oxides such as SiO<sub>2</sub>, NiO, CoO, MgAl<sub>2</sub>O<sub>4</sub>, mullite or kaolinite [1,2]. As a result of these reactions, the ceramic and metallic phases interpenetrate each other leading to the formation of a new structure named C<sup>4</sup> type (Co-Continuous-Ceramic-Composite). The produced composites with such extraordinary microstructure are characterized

by the high modulus, high strength, thermal shock resistance and low coefficient of thermal expansion [1-4]. This unique combination of desirable features is practically impossible or it is much more expensive to obtain by the conventional liquid-assisted manufacturing methods.

*In situ* production of particles reinforcing the metallic matrix is beneficial from both, technical and economical reasons. It allows for controlling the size and distribution of the second phase and is less expensive than *ex situ* production of metal-ceramic composites. However, the mechanism of the formation of C<sup>4</sup> structure is still not clear, particularly, the role of processing parameters and type of initial oxides [1-4].

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The reaction between Al and ZnO has a high negative free energy change ( $\Delta G$ ) that makes ZnO a potential candidate for the *in situ* synthesis of Al-Al<sub>2</sub>O<sub>3</sub> composites [1,2,5,6]. The experimental evidence of the redox reaction in the Al/ZnO system at the high temperature was reported in Refs. [1,2,5,6]. Following DTA analysis performed by Peng [5], this reaction is exothermic while the alumina formed in the Al-10 wt.% ZnO composite sintered at 1000°C was identified by XRD as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [5]. Moreover, in the study of Sobczak *et al* [6] on high temperature interaction between liquid aluminium and ZnO substrates, it was demonstrated that regardless the crystal structure of initial ZnO used (single- or polycrystalline), this reaction is accompanied with the formation of C<sup>4</sup> structure in the region reactively formed inside the ZnO substrate. The structural characterization of the reaction product region (RPR) revealed the large Al<sub>2</sub>O<sub>3</sub> crystals surrounded by Al phase. However, in the previous studies [1,2,6] the type of Al<sub>2</sub>O<sub>3</sub> as well as the detailed microstructure of reaction products region were not described. Based on microstructural observations in work of Sobczak [1], it was also suggested that the high-temperature interaction between the liquid Al and ZnO was affected by the strong evaporation of reactively formed Zn. As a consequence, this evaporation contributes to the enhanced transport of Al and Zn to and from the reaction front, respectively, creating favorable conditions for the redox reaction [1]. Moreover, the significant difference in the molar volume of the initial ZnO and the reactively formed Al<sub>2</sub>O<sub>3</sub> coupled with the high solubility of zinc in liquid aluminum was concluded to be responsible for the cracking of the freshly formed Al<sub>2</sub>O<sub>3</sub> interfacial layer. This resulted in the C<sup>4</sup> structure formation in the Al-Al<sub>2</sub>O<sub>3</sub> composite [1,6]. Peng *et al.* [5] reported the displacement reaction method as appropriate for the production of high quality metal-matrix Al(Zn)-Al<sub>2</sub>O<sub>3</sub> composites, in which the excessive amount of Zn was eliminated during the high temperature sintering due to strong evaporation of zinc.

The aim of this study was to perform the detailed characterization of the Al/ZnO interface at both micro- and nano-scales and to identify the type and morphology of alumina phase formed due to the interaction between liquid aluminum and ZnO[0001] single crystal.

## 2. Experimental

Pure Al (99.999%) and ZnO single crystal substrate (ZnO<sup>SC</sup>) of [0001] orientation produced by the crystal growth technology (hydrothermal method) with the surface roughness of 2 nm were used as the starting materials. The Al/ZnO<sup>SC</sup> couple was prepared in the sessile drop wettability test under dynamic vacuum produced by the continuously working turbo molecular pump as described in [6]. The first type of the Al/ZnO<sup>SC</sup> couple was produced by the contact heating procedure at 1000°C for 55 minutes. The sample was cooled after the test at the rate of  $\sim 12^\circ\text{C}/\text{min}$ . The second type of Al/ZnO<sup>SC</sup> couple was the result of the Al droplet reaction with ZnO[0001] at 1000°C for 20 minutes. However, the samples were produced by capillary purification at the test temperature and after 20 minutes the droplet was pushed to another (Al<sub>2</sub>O<sub>3</sub>) substrate that allowed to open the interface for the

further examination and to decrease the reaction between liquid Al and substrate during cooling. The samples were cooled after the test at the rate of  $\sim 14^\circ\text{C}/\text{min}$ .

The microstructure of the Al/ZnO<sup>SC</sup> couple was examined with Philips XL 30 Scanning Electron Microscope (SEM) equipped with the Link ISIS (Oxford Instruments) an energy dispersive X-ray (EDX) spectrometer which allowed to perform the quantitative point analysis.

The thin foils for the Transmission Electron Microscopy (TEM) observations were prepared in a FEI Quanta 3D microscope using Focused Ion Beam (FIB) technique. This allowed for the samples to be obtained from a required location. The TEM examinations were carried out using TECNAI G<sup>2</sup> FEG super TWIN (200 kV) microscope equipped with High Angle Annular Dark Field (HAADF) detector and integrated with an EDAX energy dispersive X-ray spectroscopy system. The selected area electron diffraction patterns (SAED) were obtained using TEM Philips CM 20 Twin (200 kV) and previously mentioned instrument.

## 3. Results and discussion

The SEM microstructure of the reactively formed area called reaction product region (RPR) created due to the interaction of ZnO[0001] single crystals at 1000°C is presented in Fig. 1. It is visible that round and large crystals of max.  $\sim 20\ \mu\text{m}$  size are located at the Al/ZnO interface (Figs. 1a,b). The presence of the individual crystals inside the droplet was also noticed (Fig. 1c). On the other hand, under higher magnification in the backscattered electron mode of observation, slightly different contrast at the ZnO edge was visible (Fig. 1d). As it was expected, the EDX elemental analysis proved that those large crystals were the Al<sub>2</sub>O<sub>3</sub> surrounded by the Al channels with dissolved Zn.

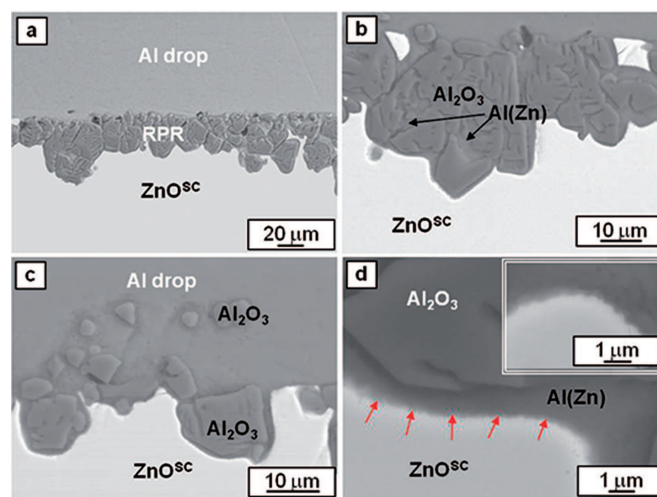


Fig. 1. SEM micrographs (backscattered electrons mode) of the reaction product region formed due to the interaction between the molten aluminum and ZnO(1000) single crystal at 1000°C: general view (a), shape and size of the large crystals forming interpenetrating network with the metallic channels (b), presence of the individual crystals inside the droplet (c) and ZnO edge exhibiting different contrast (d)

The alumina crystals obtained in our study are much larger in size than those reported for other reactive Al/oxide sys-

tems (NiO, CoO, ZrO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, B<sub>13</sub>O<sub>2</sub>, mullite, kaoline, fly ash) in the comparable temperature range of 700-1000°C [1,2]. Following explanation given by Sobczak in [1], such a large crystal size can be explained by taking into account the extraordinary high volumetric mismatch between the initial oxide of Zn and reactively formed alumina (14.28 and 25.62 cm<sup>3</sup>/mol, respectively [7]) and the fact that according to the reaction:  $2\text{Al} + 3\text{ZnO} = \text{Al}_2\text{O}_3 + 3\text{Zn}$ , the transformation of three moles of ZnO leads to the appearance of one mole of Al<sub>2</sub>O<sub>3</sub>. As it was calculated in Ref. [7], this process entails ~40% reduction in volume, which causes differential strains, breakage of freshly formed Al<sub>2</sub>O<sub>3</sub> interfacial layer and the formation of wide discontinuities in the layer. Also, intensive zinc evaporation can contribute to the growth of such extraordinary large Al<sub>2</sub>O<sub>3</sub> crystals.

The observations of these very large alumina crystals are in opposition to the results of the interaction between aluminum and other single crystal substrates such as CoO and NiO, both of [100] orientation [1,9], for which the calculated volume reduction is 24% and 15%, respectively [7]. In the Al/CoO [1] and Al/NiO [9] couples, the alumina was in the shape of nanosized precipitates located both within the substrate and the drop due to cleaving and fragmentation of the reaction product region initially formed inside the CoO and NiO single crystal substrates and next movement of delaminated fragments into liquid drop. Moreover, the reaction product region possessed a layered structure that was suggested to be related with the formation of the intermetallic phases in these systems. According to the proposed mechanism [1], in the first stage, the breakage of alumina layer takes place caused by the volumetric mismatch between the oxide substrate and the new Al<sub>2</sub>O<sub>3</sub>. During the second stage, the reaction between the produced metal (Co or Ni) and liquid aluminum leads to the formation of intermetallic phases such as Al<sub>3</sub>Ni, Al<sub>9</sub>Co<sub>2</sub>, Al<sub>13</sub>Co<sub>4</sub> within the channels between the alumina. This process is accompanied with the volume increase resulting in meaningful stresses, cracks in the RPR and even the separation of RPR from the substrate. Both stages were repeated during further interaction at the high temperature thus generating the layered structure [1].

The same phase composition (Al<sub>2</sub>O<sub>3</sub> and Al) has recently been found in the RPR formed after the interaction of aluminum with polycrystalline ZnO [9]. However, that RPR layer in Al/ZnO<sup>PC</sup> was almost twice as thin and the alumina crystals were smaller (up to 10 μm) and less rounded. Analogous observations were described by Rapp *et al* [10] for the Fe/NiO reaction couple after interaction at 1000°C. In both polycrystalline and single crystal NiO substrates, the PRR consisted of the metallic Ni-Fe and FeO oxide phases interpenetrating each other. Similar to our study, the microstructure formed with polycrystalline NiO was finer, which was explained by the different reaction mechanisms at the NiO/RPR interface. Since the sintered-powder compacts of NiO revealed pores of a size that depended on the grade of initial powder, the authors [10] suggested that such pores influenced the morphology and growth of RPR during the interaction of these NiO compacts with Fe. Thus the interaction of Fe with sintered-powder compacts made from finer mesh NiO resulted in a finer RPR microstructure.

It must also be emphasized that dissimilar cooling procedures used for the preparation of Al/ZnO<sup>PC</sup> and Al/ZnO<sup>SC</sup>

couples could also affect the growth of reactively formed alumina.

The TEM examination revealed further microstructure details concerning the region of interest. It allowed also the determination of the type of alumina formed within the RPR. Figure 2a represents the bright-field image of the RPR/ZnO<sup>SC</sup> interface, where the large-dark contrasting Al<sub>2</sub>O<sub>3</sub> crystals are penetrated by the Al metallic channels. The observations at higher magnification revealed a layer of about 200 nm in thickness (Figs. 2 b,c) identified by the EDX microanalysis as the Al<sub>2</sub>O<sub>3</sub> compound. However, their SAED patterns (see Fig. 3) revealed dissimilar crystal structure of Al<sub>2</sub>O<sub>3</sub>, depending on its location in the RPR, i.e. large crystals were composed of hexagonal α-Al<sub>2</sub>O<sub>3</sub> phase with the lattice parameters of 0.476 nm and 1.299 nm while the layer was tetragonal δ-Al<sub>2</sub>O<sub>3</sub> phase of 0.56 nm and 2.337 nm lattice parameters. The same observations were performed in the case of polycrystalline ZnO<sup>PC</sup> [9]. The δ-Al<sub>2</sub>O<sub>3</sub> phase identified for the samples after longer interaction time and due to the conventional contact heating test is the transition intermediate phase in the transformation from γ-Al<sub>2</sub>O<sub>3</sub> to θ-Al<sub>2</sub>O<sub>3</sub>.

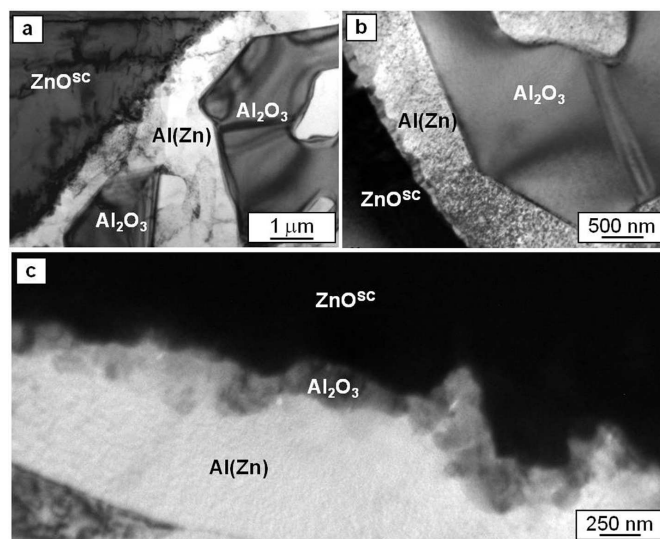


Fig. 2. TEM bright field images of the RPR/ZnO<sup>SC</sup>: general view of the RPR/ZnO interface (a); (b) and (c) the magnified areas of this interface with visible layer of Al<sub>2</sub>O<sub>3</sub> phase next to the ZnO substrate

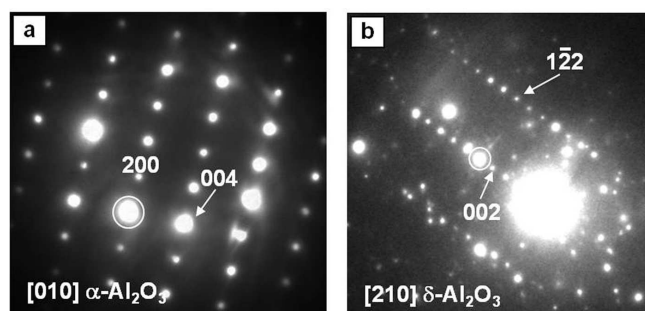


Fig. 3. SAED patterns of the α-Al<sub>2</sub>O<sub>3</sub> large crystal (a) and δ-Al<sub>2</sub>O<sub>3</sub> layer (b) presented in Fig. 2

Moreover, in that case the δ-Al<sub>2</sub>O<sub>3</sub> phase layer had dual microstructure, i.e. fine-grained crystals close to the substrate and columnar crystals growing in a direction perpendicular to the ZnO<sup>PC</sup> surface. The formation of such structure most prob-



ably took place during the cooling and it could be compared to the chill and columnar zones of the ingot cross-section. In the Al/ZnO<sup>SC</sup> specimens, this effect was less evident and the  $\delta$ -Al<sub>2</sub>O<sub>3</sub> layer consisted of smaller crystals without any discontinuities.

In the reactive Al/oxide systems, beside the type of initial oxide, the alumina type formed within the RPR depends on at least two factors. The first one is the crystallographic orientation of the initial reactive oxide, as it was demonstrated by Shen *et al* [11] on example of high temperature interaction between liquid aluminum and MgO single crystal substrates in the sessile drop tests [11]. By applying XRD characterization Shen *et al* evidenced the formation of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with MgO single crystals of [100] orientation while for [110] and [111] orientations, the  $\kappa$ ,  $\kappa'$  and  $\delta$  phases were identified. However, recent TEM studies considering the interaction between molten aluminum and MgO single crystal of [100], [110] and [111] orientation reported in [12] by Morgiel *et al* evidenced that always  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was formed independently on crystal structure orientation of MgO used in the sessile drop tests. The fabrication temperature is the second factor affecting the type of reactively formed oxide, as reported by Yoshikawa *et al* [13]. They applied the X-ray diffraction technique to examine the Al/SiO<sub>2</sub> couples produced due to the immersion of SiO<sub>2</sub> rods in molten aluminum over a temperature range of 800-1100°C. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was found to be the main component in the samples produced at temperatures above 1000°C, while at 800°C < T < 1000°C, the fine-grained  $\theta$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (subsequently and isothermally transformed into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and coarse-grained  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formed [13]. On the other hand, TEM studies of AlCu/SiO<sub>2</sub> couple obtained in classical sessile drop experiment performed in a vacuum at 900°C between the aluminum-copper alloy (Al-16.7 at.% Cu) and SiO<sub>2</sub> (amorphous) substrate led to the formation of two types of alumina – alpha and delta [14].

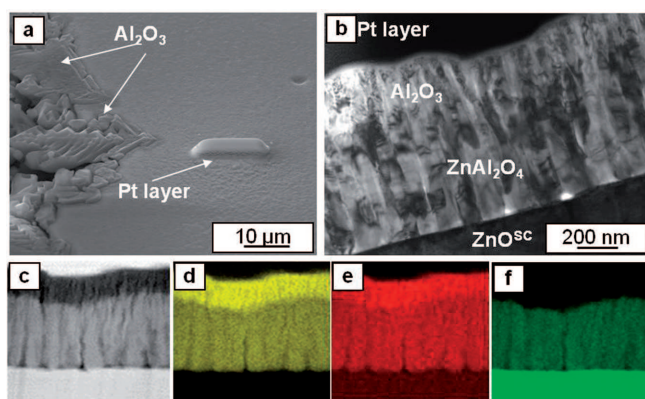


Fig. 4. SEM image of the sample surface after the pushing drop test at 1000°C for 20 min with the protective platinum layer resulting from the foil preparation with FIB (a) together with TEM bright field image of the RPR/ZnO(0001) with visible layers of Al<sub>2</sub>O<sub>3</sub> and ZnAl<sub>2</sub>O<sub>4</sub>. Figure 4c presents the STEM image together with the map of element distribution Al-K (d), O-K (e) and Zn-K (f) recorded for this area

In this study the formation of the thin layer of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> was presumed to be an effect of cooling. To confirm this statement experiment applying the pushing drop procedure was performed which allowed to uncover the interface between the droplet and reactively formed products. Moreover, the dif-

fusion of elements from and to reaction front and evaporation of Zn from drop were blocked after the removal of the drop from substrate. General view of this area is visible in Fig. 4a where occasionally large alumina dendrites are present. The TEM examination of the lamella cut from the contact area showed the fine columnar grains growing in the perpendicular direction to the substrate (Fig. 4b). Moreover, under scanning transmission mode the different contrast of these crystals was observed. The map of element distribution, such as that presented in Figs. 4c-e, as well as the chemical point analysis revealed the presence of both Al<sub>2</sub>O<sub>3</sub> and ZnAl<sub>2</sub>O<sub>4</sub> spinel.

The particular interest was taken to identify the type of reactively formed alumina. Many selected area diffraction patterns as well as the high resolution images (see example in Fig. 5) were taken in order to determine the alumina type.

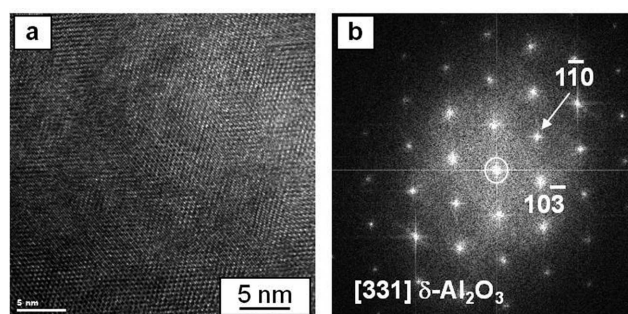


Fig. 5. HREM image of the  $\delta$ -Al<sub>2</sub>O<sub>3</sub> crystal of (331) orientation (a) together with its Fast Fourier Transform (b)

The thin columnar layers, often placed one after another, caused the difficulties in detailed TEM characterization. Among various possible forms of Al<sub>2</sub>O<sub>3</sub> reported in Ref. [15] the best agreement was noted for the  $\delta$ -Al<sub>2</sub>O<sub>3</sub> phase.

#### 4. Summary

The reaction between the liquid aluminum and ZnO<sup>SC</sup> substrate of [0001] crystallographic orientation at a temperature of 1000°C under vacuum led to the formation of the C<sup>4</sup> type reaction product region (RPR) of about 50  $\mu$ m in thickness. It consisted of the extraordinary large Al<sub>2</sub>O<sub>3</sub> crystals interpenetrated by the Al(Zn) metallic channels. Moreover, the formation of the thin alumina layer at the ZnO<sup>SC</sup>-side interface was also detected using the TEM technique. Its growth was presumed to be an effect of cooling.

The alumina present within the reaction product region was of different types with respect to the morphology and localization. The large crystals were identified as the hexagonal  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase and they were the main constituent of the RPR, while the  $\delta$ -Al<sub>2</sub>O<sub>3</sub> phase was present in the RPR/ZnO<sup>SC</sup> interfacial layer. Most probably large volume reduction for Al/ZnO system and also contribution of the intensive zinc evaporation is responsible for such extraordinary large  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals. The application of modified sessile drop method using pushing drop procedure allowed to reveal the formation of fine crystalline alumina and ZnAl<sub>2</sub>O<sub>4</sub> spinel. Nevertheless, the alumina type created in the reaction was difficult to identify due to its fine columnar structure as both variants: gamma and delta were possible, however, the best fit was observed for  $\delta$ -Al<sub>2</sub>O<sub>3</sub> phase.

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