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High-temperature reactivity and wetting characteristics of Al/ZnO system related to the zinc oxide single crystal orientation

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Abstract Wettability and reactivity of the Al/ZnO couple at a temperature of 1273 K in vacuum have been studied with application of modified sessile drop method. The results obtained for the ZnO single crystal substrates of various orientations evidenced non-wetting by liquid aluminium, showing high contact angles of 100°–107°. Detailed transmission electron microscopy characterization unambiguously proved that the creation of two interfacial layers revealing highly epitaxial growth took place at high-temperature interaction between liquid Al drop and ZnO substrate. The layers of columnar grains consisted of reactively formed Al_2O_3 and $ZnAl_2O_4$, the second one growing at the expense of the alumina. The alumina was identified as either cubic γ-, tetragonal δ- or monoclinic λ-Al_2O_3, depending on subtle changes in chemistry of the surface top layer of the ZnO substrates.

Introduction

Light-weight Al–Al_2O_3 composites produced in situ due to redox reaction between liquid Al and oxides such as SiO_2, mullite, kaolinite, CeO_2, NiO, MgO and ZnO are attractive alternative for conventional light alloys used in aviation and ground transport industry [1–6]. That is why, there is a strong need to extend the knowledge on both reactivity and wettability of these systems of interest. The sessile drop experiment is of particular usefulness in such studies and was successfully applied previously to Al/SiO_2 [1], Al/NiO [3, 4], Al/MgO [5], Al/ZnO [6–8] and Al/Y_2O_3 [9] systems. The last two systems reveal similarities, since the reactively formed aluminium oxide crystallites are large and surrounded by the metallic channels composed of either Al(Mg) or Al(Zn). These two systems can find an application when the higher content of alumina is desired, and larger amount of metal is predictably reduced, as one way to control the quantity of the alloying element is by using MeO, which produces Me in a vapour form by the redox reaction with Al. Zinc and magnesium oxides fulfil this requirement. The experiment performed at 1273 K leads to the formation of reaction product region (RPR) composed of alumina particles interpenetrated by the metallic channels being either Al(Mg) or Al(Zn). In the RPR, the alumina content can be increased, while the zinc or magnesium is kept low in these metallic channels because of its diffusion into the drop followed by further vaporization from the liquid Al(Zn) or Al(Mg) metal. So far, several researchers have used zinc oxide for in situ reactive synthesis of Al–Al_2O_3 composites [9–13].

The structural investigation of Al/ZnO^{SC} sessile drop couples reported in works [7, 8] revealed the formation of not only large α-Al_2O_3 crystals interpenetrated by the Al(Zn) channels but also an additional thin layer located

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next to the ZnO substrate. In study [6], the examination performed on polycrystalline ZnO substrate reacting with molten aluminium established the occurrence of thin layer of about 250 nm specified as metastable δ-Al_2O_3. In the next paper, the application of the same sample preparation procedure but using the single crystal ZnO substrate of ⟨0001⟩ orientation (further denoted as $ZnO^{\langle 0001\rangle}$) was reported. The creation of the thin alumina layer at the ZnO-side interface was also detected using the transmission electron microscopy (TEM). At that moment, its growth was presumed to be an effect of cooling [8]. In order to confirm this statement, the Al/ZnO couple was produced by capillary purification (CP) procedure combined with drop pushing procedure (DP) described in [14]. Such a unique procedure comprises squeezing of the liquid aluminium from the capillary on the substrate surface at the test temperature of 1273 K, followed by pushing it into another location of the substrate after appropriate contact time. Several advantages arose from the experiment performed in such a way. At first, it allowed non-contact heating of both Al and ZnO materials and, therefore, to avoid the effect of heating history due to the interaction between them during contact heating to the test temperature, commonly used in wettability tests. Next, it caused the removal of the primary oxide film from the Al drop directly in the high-temperature chamber under vacuum. And finally, it helped to exclude or at least significantly reduce the effect of the cooling history, as the droplet was no more in contact with the substrate during the cooling. Three phases were detected within the Al/$ZnO^{\langle 1-100\rangle}$ couple: locally distributed large crystals of α-Al_2O_3, the alumina of unknown type and $ZnAl_2O_4$ spinel placed between the unknown Al_2O_3 and ZnO. Both alumina and spinel took form of columnar grains, which placed one above other formed thin and continuous layer of about 200 nm in thickness [7]. The above results as well as incomplete literature data require systematic examination of the Al/ZnO contact system comprising of both the reactivity and wettability strongly correlated with the substrate surface structure, which was the aim of the research presented here. The systematic studies with application of the pushing drop procedure and various crystallographic orientations of the ZnO substrate were performed first time ever.

Experimental

Aluminium of 99.999 % purity and ZnO single crystal substrates were subjected to the sessile drop wettability tests at 1273 K using experimental facility described in details in work [14]. All samples were ultrasonically cleaned in the isopropanol before the test. Zinc oxide single crystals ZnO^{SC} of ⟨1−100⟩, ⟨1−120⟩, and ⟨0001⟩ orientations and of two variants of atomic termination of the ZnO surface (denoted as $ZnO^{\langle 0001\rangle Zn}$ or $ZnO^{\langle 0001\rangle O}$ for Zn-terminated and O-terminated surfaces, respectively) are grown by hydrothermal method under high pressure with the surface roughness less than 5 Å.

As the experimental conditions have significant influence on the wetting test results [15], two testing procedures were applied in the sessile drop wettability tests: (1) CP and (2) drop pushing in order to expose the Al/ZnO interface at high temperature directly in vacuum chamber after appropriate interaction time and uncover freshly formed reaction products for further SPM and TEM investigation. It consisted of squeezing the aluminium droplet through an alumina capillary at the test temperature and its deposition on the ZnO substrate. After 20 min of Al–ZnO interaction, the drop was transferred to a new location of the same ZnO substrate for another 5 min contact and then finally pushed away from the substrate to the alumina support placed next to the ZnO single crystal [14]. After wettability tests, the Al/ZnO couples were cooled at the rate of ~10 K/min. All the manipulations were undertaken under dynamic vacuum produced by the continuously working turbomolecular pump.

The TEM lamellas were obtained using focused ion beam technique (Quanta 3D, FEI) and in situ lift out technique, which guaranteed the precise probing of the place of analyses. The TEM techniques comprising of bright-field (BF), high-resolution observation and also selected area electron diffraction (SAED) were carried out using TECNAI G2 FEG super TWIN (200 kV) microscope. Additionally, high-angle annular dark-field detector allowed the observation in the scanning transmission mode and an energy dispersive X-ray spectroscopy system manufactured by EDAX company integrated with the microscope let to carry out the local chemical analyses as well as to collect the maps of element distribution in the particular location in the sessile drop sample.

Results and discussion

Wettability tests

The contact angle measurements of aluminium on ZnO^{SC} substrates of ⟨1−100⟩, ⟨1−120⟩ and ⟨0001⟩ (Zn or O faced) orientations were carried out at 1273 K for 20 min. The obtained results (Fig. 1a and Table 1) indicate that interaction of liquid aluminium with all ZnO substrates exhibits non-wetting behaviour ($\theta > 90°$), reaching the contact angle values of $\theta = 100–107°$.

The wetting kinetics of the drop pushed away to another location at the same substrate has been also studied for 5 min. As can be seen in Fig. 1b for the ZnO ⟨0001⟩

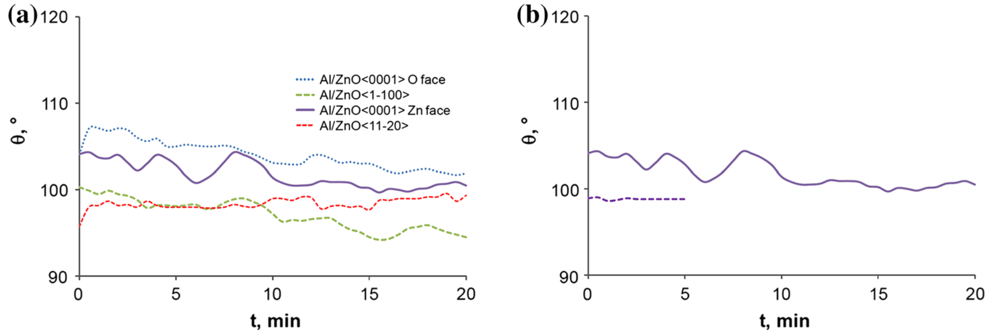

Fig. 1 Wetting kinetics of Al/ZnO^{SC} system measured at first location of the Al drop on the ZnO substrate at 1273 K lasting for 20 min, in which ZnO substrates of various orientations, $\langle 0001\rangle$ of two variants O or Zn faced, $\langle 1-100\rangle$ and $\langle 1-120\rangle$, were applied (**a**). Comparison of the wetting angle changes for the drop placed at first (20 min at 1273 K) and second (5 min at 1273 K) location of the same ZnO $\langle 0001\rangle^{Zn}$ substrate (**b**)

Table 1 Approximate thickness values of alumina and spinel layers formed due to the interaction between aluminium and ZnO single crystal of various orientation after 5 and 20 min in 1273 K as well as the type of formed Al_2O_3

Couple	Testing conditions		Contact angle (°)				Time of interaction (min) at 1273 K	Thickness (nm) of Al_2O_3	Thickness (nm) of $ZnAl_2O_4$	Type of A_2O_3
	Time (min)	Temp (K)	$T = 0$ min		$T = 20$ min					
			θ left	θ right	θ left	θ right				
Al/ZnO$^{\langle 0001\rangle Zn}$	20 + 5	1273	105.1	103.4	103.6	97.5	20	150	600	δ or γ
	5	1273	96.3	101.6	95.0	103.3	5	350	400	δ or γ
Al/ZnO$^{\langle 0001\rangle O}$	20 + 5	1273	101.0	101.3	102.0	101.7	20	300	500	δ
	5	1273	95.9	100.0	91.8	95.1	5	400	400	λ
Al/ZnO$^{\langle 1-100\rangle\ Zn}$	20 + 5	1273	101.9	99.0	96.0	93.1	20	200	550	γ, δ, λ
	5	1273	1*	1*	1*	1*	5	150	200	γ, δ, λ
Al/ZnO$^{\langle 11-20\rangle Zn}$	20 + 5	1273	90.6	101.1	100.6	98.6	20	180	1000	δ or γ
	5	1273	2*	2*	2*	2*	5	350	280	δ or γ

1* sticking of the drop to the pusher making impossible to calculate the contact angles

2* drop too big to push it to another place on substrate

substrate, no change in the contact angle value took place in comparison with the first position of the drop on the substrate. The contact angle formed on ZnO $\langle 0001\rangle$ surface was lower by 6°, reaching the value of 99°. The dissimilar wetting behaviour of the Al drop in the first and second positions on the same substrate might be related to the effect of liquid metal saturation with oxygen and zinc during first 20 min contact, resulting in a suppressed interaction between the fresh substrate surface and the Al(O, Zn) drop in its second position after it was moved.

The tendency to lower the contact angle value with time of interaction can be associated with either the evaporation from the drop or due to chemical reaction, which takes place at the drop/substrate interface under experimental conditions used. First phenomenon can be excluded by the measurements of the diameter ($d_{\max}$) and height ($h_{\max}$) of the drop at the beginning and at the end of the contact angle measurements. During the performed experiment, $d_{\max}$ increased with decreasing $h_{\max}$, while the corresponding drop volume changed up to 0.2 % only, which clearly evidenced that although the metal evaporation takes place, its effect on the drop size is negligible. Therefore, it was presumed that lowering of the contact angle is caused by the formation of the new compound at the drop/substrate interface.

The literature data suffer from very limited information concerning both the wettability and reactivity in Al/ZnO system followed by the detailed microstructure and phase composition characterization. The presented results can be compared with those reported by Sobczak et al. [1, 16] showing high reactivity accompanied with a lack of wettability in the Al/ZnO couple. High contact angles

($\theta = 111$ for single crystalline substrate and $\theta = 140$ for polycrystalline substrate) were measured at 1273 K. At that temperature, the Al_2O_3 reaction product, suggested by the electron microscopy characterization coupled with EDS analysis, is known to be wetted by molten Al, as reported in the analysis of literature data on contact angle measurements of Al/Al_2O_3 system performed by Sobczak et al. [17]. Since the removal of oxide film from Al drop did not improve the wettability in Al/ZnO couple, its non-wetting behaviour was explained either by secondary roughening of initially smooth ZnO single crystal surface or by secondary oxidation of the Al drop surface [1]. The first explanation came from the observation of the fine alumina precipitates detected at the substrate surface around the Al drop and probably created by evaporative-reactive deposition caused by enlarged transport of Al vapour under UHV and its reaction with ZnO. The idea of secondary oxidation of the drop surface was based on the observations of fine alumina precipitates at the drop surface, particularly densely localized close to the triple line. Their formation was explained by enhanced transfer of oxygen from the ZnO substrate caused by copious evaporation of Zn. It should be highlighted also that in previous reports, no information about the type of reactively formed alumina was provided, while the results obtained were compared with experimental data showing wetting in the Al/Al_2O_3 couple at 1273 K when α-Al_2O_3 was used. Following more recent reports by Shen et al. [18–21] concerning the influence of the α-Al_2O_3 single crystal orientation on wetting its surface by molten aluminium in the temperature range of 800–1500 °C, it can be found that this effect is very strong. The wetting of molten Al on differently oriented single crystals $R\langle 0112\rangle$, $A\langle 1120\rangle$ and $C\langle 0001\rangle$ showed that the adhesion of the molten aluminium on the R and A surfaces is much stronger in comparison with the C surface.

Therefore, in this study, the detailed structural investigation was performed using two advanced techniques of materials characterization, i.e. the scanning probe microscopy (SPM) technique (in order to examine the subtle changes in substrate surface topography after high-temperature contact with liquid Al), followed by the transmission electron microscopy examination of the microstructure and phase composition of the compounds present at the drop/substrate interface.

Substrate surface topography after interaction with Al drop

Figure 2a shows the image of the $ZnO^{\langle 11-20\rangle}$ surface exposed at high temperature after interaction with aluminium. There are five characteristic areas that can be distinguished. Regions 1 and 2 correspond to the place of the first contact of the Al drop with ZnO substrate. Region 3 represents the triple line region formed after 20 min of interaction. Region 4 is just outside of the contact place, while the fifth region is far away from it. During dropping the aluminium from the capillary, the volume of the squeezed drop slightly increases. Each ring marked with arrows visible in Fig. 2a corresponds to the new volume.

Figure 2b–f shows the series of measurements performed consequently for all mentioned above regions. First region (Fig. 2b) reveals the dramatic change of the substrate structure although the contact time was extremely short and lasted only few seconds. It resulted in the immediate reduction of the ZnO by liquid Al. The presence of the triple line, of about 100 nm depth, can be also noted here. The region in contact with the Al is composed of many craters along which the liquid aluminium can infiltrate the monocrystalline substrate and reactively formed products can appear.

The examination of region 2 (Fig. 2c) confirmed the presence of large channels through which the transfer of liquid Al to the reaction front and reactively formed zinc to the drop took place. The maximum depth of these channels was 140 nm. Region 3 visualized in Fig. 2d is the surface topography after extra dropping of aluminium. This structure is different from the previous one because of lack of large craters and the occurrence of fine columnar crystals within this area. Also the RPR is located much lower than the place outside the drop. The dissolution of the ZnO substrate in the drop results in the formation of the characteristic crater about 700 nm deep in the triple line area. Furthermore, in region 4 (Fig. 2e), representing the area beside the drop/substrate contact, the secondary roughening of the surface can be observed contrary to the flat surface of the zinc oxide ($R_a = 2$ nm) measured far away from the place of Al/ZnO contact (Fig. 2f). This phenomenon takes place at 1273 K due to chemical reaction between Al vapour and ZnO substrate surface, and it can contribute to the formation of high apparent contact angles as explained in [1].

Microstructure and phase composition of the products reactively formed at the drop/substrate interface

The surface of the ZnO substrates after high-temperature interaction with molten aluminium was next observed with scanning electron microscopy (Fig. 3). Figure 3a shows the overall view of the sample obtained in DP. The places where the aluminium drop contacted the substrate for 20 min (the first position) and 5 min (the second position) are well distinguishable as the circles of brighter contrasts. The local existence of large crystals, previously identified as α-Al_2O_3 [7], can be noticed (Fig. 3b). They appeared due to the interaction of ZnO substrate with so-called

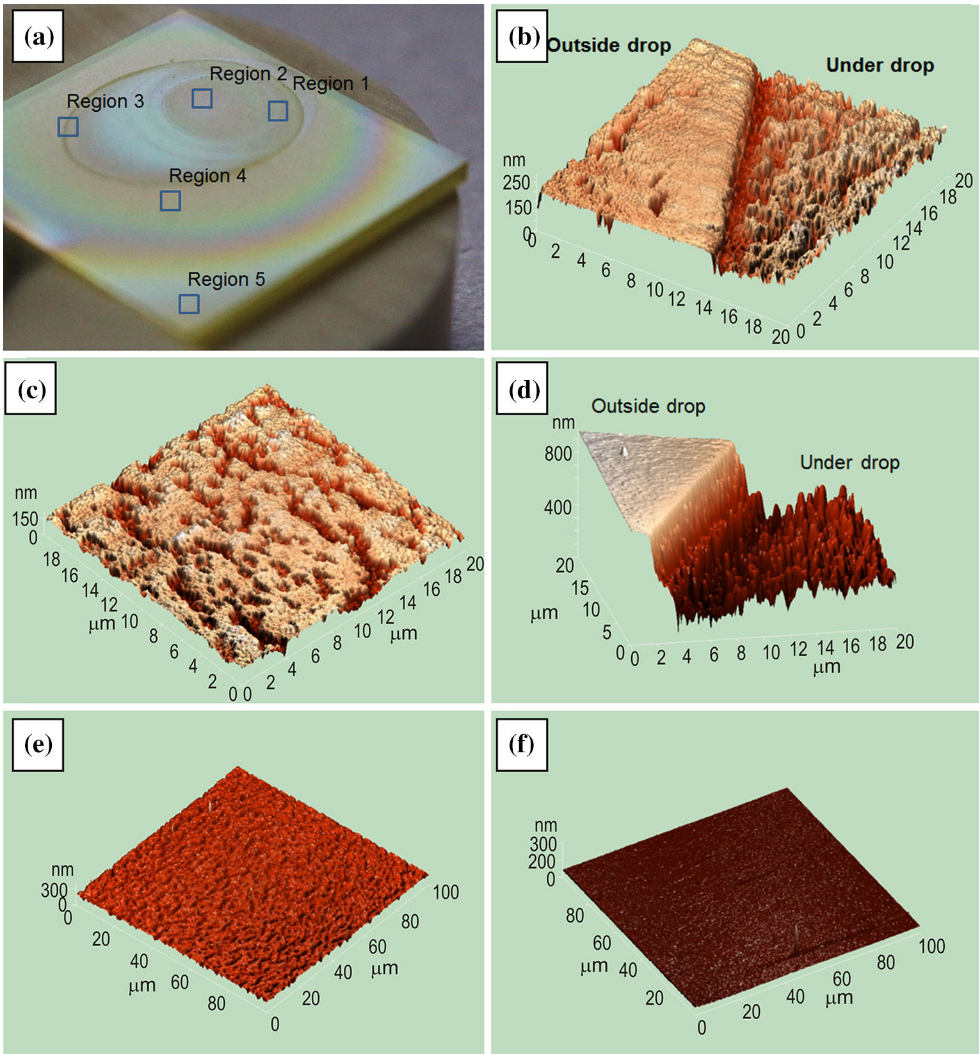

Fig. 2 SPM images of the ZnO$^{\langle 11-20\rangle}$ surface exposed at high temperature after interaction with aluminium: general view of the sample surface with particular areas of interest (**a**). Region 1 and 2 denotes the first contact of the Al drop with ZnO substrate (**b**, **c**), region 3 represents the triple line region formed after 20 min of interaction (**d**), region 4–surface area close but beyond the contact with the drop (**e**) and region 5 is far away from it (**f**)

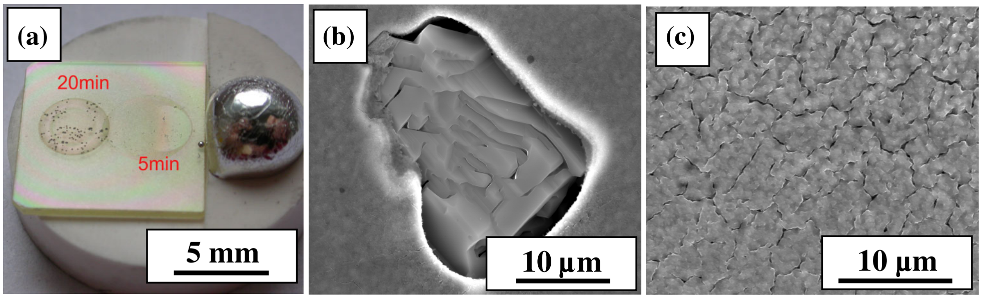

Fig. 3 Overall view of the Al/ZnO sessile drop sample on alumina support after using drop pushing procedure. Al drop was removed from ZnO substrate onto alumina support (**a**). SEM-SE *top view* image of the substrate surface with visible large dendrites of α-Al_2O_3 locally distributed on the substrate surface corresponding to the first position of the drop contacting ZnO for 20 min (**b**) and area of contact close to large dendrites (**c**)

"daughter" droplets, which remained after pushing off the "mother" drop.

In all cross-sectioned Al/ZnO couples, the formation of two layers revealing strong epitaxial growth was observed in the following order: ZnO/$ZnAl_2O_4$/Al_2O_3. Both the spinel and aluminium oxide took the shape of long, columnar crystals, of which the acquisition of either the electron diffraction or high-resolution image was not a trivial task because of their mutual overlapping.

Figure 4 shows the microstructure of the cross-sectioned area within the places where Al drop reacted for particular time—the first lasting 20 min and the second for another 5 min (total of 20 + 5 min) with $\langle 0001\rangle$-oriented ZnO- and Zn-faced substrates. As it can be noticed in Fig. 4a, e, a layer of columnar grains can be distinguished above the $ZnO^{\langle 0001\rangle Zn}$. Observations in scanning transmission mode (Fig. 4f, g) revealed various contrast within this layer. The EDS analysis showed the presence of alumina and $ZnAl_2O_4$ spinel. This last compound was observed between Al_2O_3 and ZnO. For the Zn-terminated $\langle 0001\rangle$ orientation of ZnO single crystal, the approximate thicknesses of reactively formed layers after interaction at the first location of the drop on the substrate (20 min time) were 150 and 600 nm, and in the second location (another 5 min), they were 350- and 400-nm thick, for the alumina and spinel, respectively. In contrary to this, when the top layer of the single crystal consisted of the oxygen atoms ($ZnO^{\langle 0001\rangle O}$), the thicknesses of both products after 20 min of the interaction were 300 nm (Al_2O_3) and 500 nm ($ZnAl_2O_4$), while at the second location of the drop (5 min of reaction at 1273 K), they were similar and both of about 400 nm (Fig. 5).

Particular attention was paid to the determination of the type of formed aluminium oxide. The analysis of the SEAD patterns showed that the crystal structure of Al_2O_3, formed after 20 min interaction of aluminium with $ZnO^{\langle 0001\rangle Zn}$, was either γ- or δ-$Al_2O_3$ phase, while for the $ZnO^{\langle 0001\rangle O}$, the columnar grains of tetragonal phase delta prevailed. At the second location of the drop, the drop/substrate interaction was different for the applied two variants of the single crystal. In the case of the top surface layer composed of zinc atoms, the appearance of γ- or δ-Al_2O_3 was observed, wherein the orientation of the gamma oxide was the same as that of spinel (Fig. 4b–d). Conversely, the monoclinic λ-Al_2O_3 phase was mostly formed for the samples with the top layer of ZnO single crystal built of oxygen atoms (Fig. 5a–c).

Interaction of molten aluminium and ZnO of $\langle 1{-}100\rangle$ orientation (Fig. 6a, b) resulted in the appearance of the aluminium oxide and the spinel of 200 and 550 nm in thickness (after 20 min) and 150 and 200 nm (after 5 min). However, the most spectacular difference in the thickness of these two layers was observed for the ZnO substrate of $\langle 1{-}120\rangle$ orientation (Fig. 4c, d), where after 20 min of interaction, the aluminium oxide thickness was only 180 nm, while that of spinel increased up to 1000 nm. After 5 min of interaction, the widths were similar and reached 350 nm (aluminium oxide) and 280 nm (spinel). The reaction of $\langle 1{-}120\rangle$-oriented ZnO single crystal and

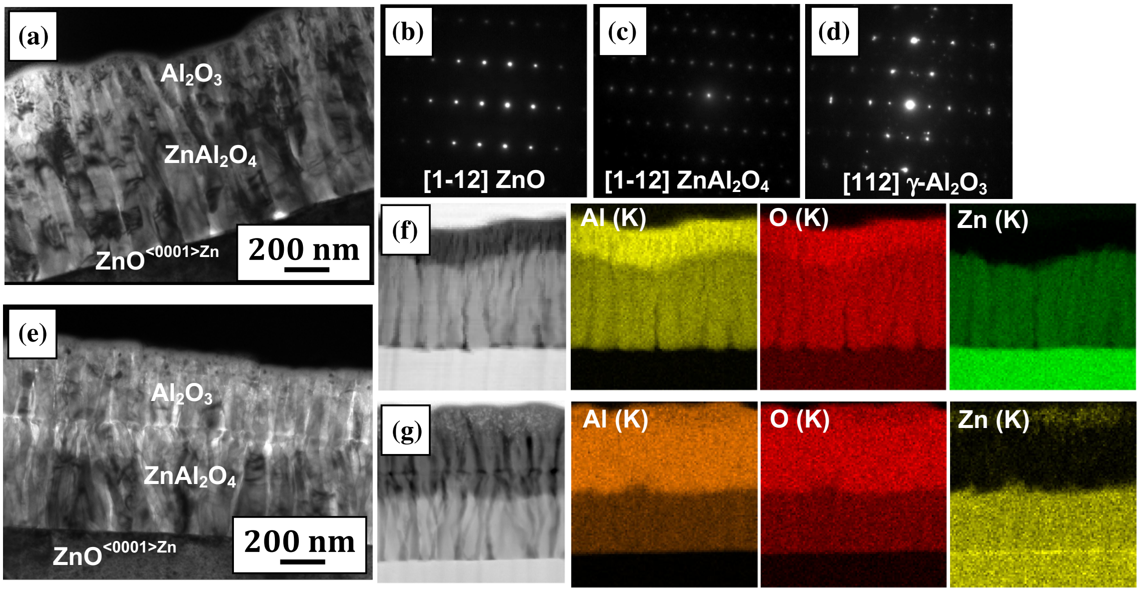

Fig. 4 TEM-BF image of the RPR/$ZnO^{\langle 0001\rangle Zn}$ with visible layers of Al_2O_3 and $ZnAl_2O_4$ formed after 20 min of drop/substrate contact at 1273 K (**a**) and the one created at second location of the drop staying in contact with the substrate for another 5 min time (**e**) of interaction with Al at 1273 K. **b–d** shows the SAED patterns of the ZnO, $ZnAl_2O_4$ and Al_2O_3 crystals, respectively. **f** and **g** present the STEM images together with the map of element distribution Al, O and Zn recorded for the RPR formed at first and second location of the drop on the $ZnO^{\langle 0001\rangle Zn}$ substrate, respectively

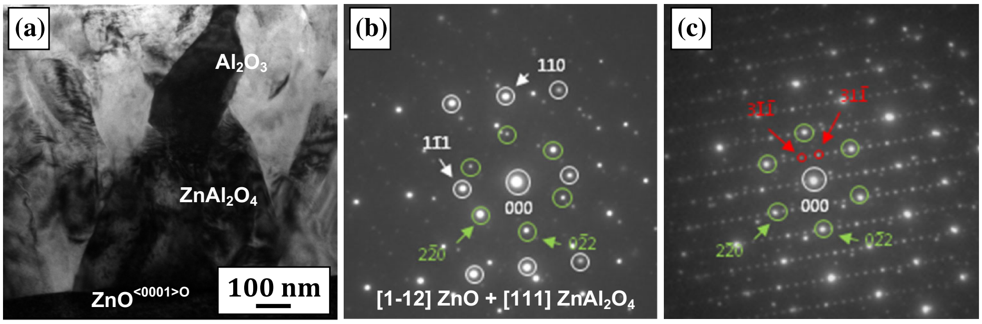

Fig. 5 TEM-BF image of the RPR/$ZnO^{\langle 0001\rangle O}$ with Al_2O_3 and $ZnAl_2O_4$ crystals formed after 5 min of interaction of ZnO with Al drop at 1273 K (**a**). **b** and **c** show the SAED patterns of the ZnO together with $ZnAl_2O_4$ (**b**) and $ZnAl_2O_4$ with Al_2O_3 crystals (**c**)

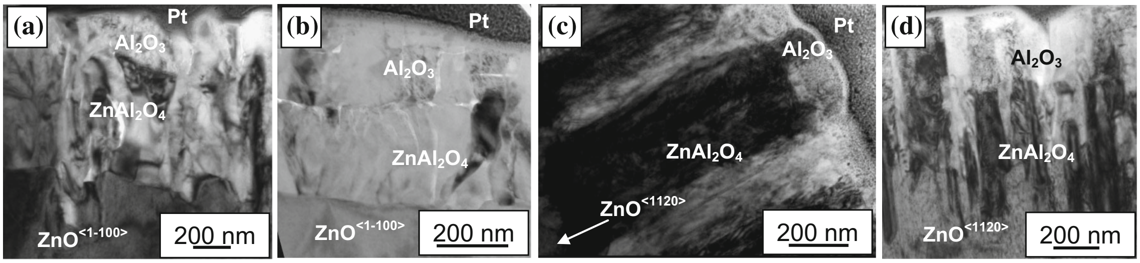

Fig. 6 TEM-BF images of the RPR/$ZnO^{\langle 1-100\rangle}$ cross section with Al_2O_3 and $ZnAl_2O_4$ crystals formed after 20 min (**a**) and 5 min (**b**) of interaction with Al at 1273 K together with BF images of the RPR/$ZnO^{\langle 1-120\rangle}$ with Al_2O_3 and $ZnAl_2O_4$ crystals formed after 20 min (**c**) and 5 min (**d**) of interaction time

aluminium at 1273 K for both 20 and 5 min led to the formation of γ- or δ-Al_2O_3 but the gamma alumina dominated for the second interaction (Fig. 7). On the other hand, the research performed on sample Al/$ZnO^{\langle 1-100\rangle}$ has shown the presence of all three of the mentioned variations of metastable alumina γ-, δ- or λ-Al_2O_3. The comparison of thickness of both alumina and spinel layers as well as the type of formed Al_2O_3 has been presented in Table 1.

As it can be easily noticed, subtle changes of the top surface chemistry of the ZnO substrate influence the type of created alumina phase as well as the thickness of both alumina and spinel. The largest thickness was obtained in the case of spinel formed after the reaction with ZnO of ⟨11–20⟩ orientation. However, it should be also pointed that these phase composition changes do not cause the changes in the contact angle values, which are almost the same in all the cases and are in fact the contact angle between the aluminium and metastable alumina. The morphology of the alumina takes shape of longitudinal columnar grains in all the cases—also visible under SPM. The potential of the C4 morphology creation (co-continuous ceramic composite composed of mutually interpenetrated metallic and ceramic phases) was previously attributed to the volume mismatch between the substrate (ZnO) and reactively formed alumina that was believed to be α-Al_2O_3, being as large as 40 % [22]. Such a type of morphology occurs after long time of interaction, when the reactively formed product is dominated by alumina interpenetrated with Al(Zn). Short time of interaction results in creation of two products: alumina and spinel in the form of layers one above the other. The question that arises is which route of creation of the products among the two proposed below takes place in this study? The analysis of experimental results suggests that the reactively changed interfaces can be formed by two possible sequences (single slash denotes stable and double slash denotes unstable interface):

$$\begin{aligned} \mathrm{Al//ZnO} &\rightarrow \mathrm{Al/Al_2O_3//ZnO} \\ &\rightarrow \mathrm{Al/Al_2O_3/ZnAl_2O_4/ZnO} \end{aligned} \quad (1)$$

or

$$\begin{aligned} \mathrm{Al//ZnO} &\rightarrow \mathrm{Al//ZnAl_2O_4/ZnO} \\ &\rightarrow \mathrm{Al/Al_2O_3/ZnAl_2O_4/ZnO} \end{aligned} \quad (2)$$

The results in Table 1 confirm that the growth of the spinel (especially pronounced in the case of ⟨11–20⟩ orientation) is favoured during the first contact of the aluminium with zinc oxide, when the drop is not saturated with the oxygen and zinc. After interaction in the first location, the chemical composition of the drop changes and in its second location, the drop becomes less reactive in contact with fresh ZnO surface. Therefore, the reactively formed alumina and spinel are of more or less of the same thickness. Taking into account the time of interaction at the first location (20 min of contact plus another 5 min, when the drop is placed and kept at the second location before it is pushed away) and the second one (5 min only) and

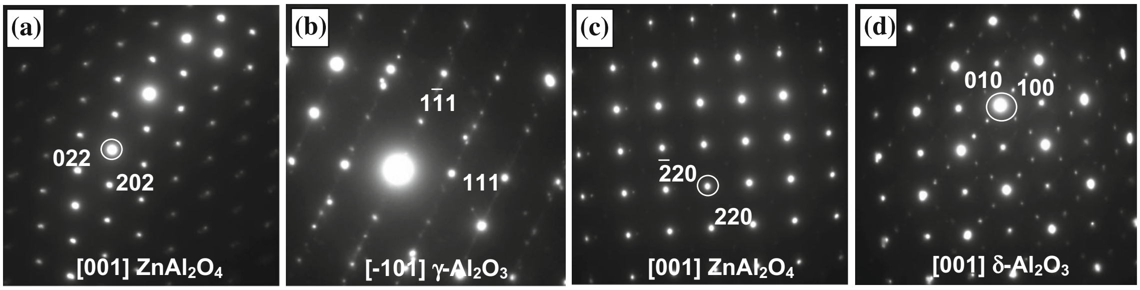

Fig. 7 SAED patterns of the $ZnAl_2O_4$ and Al_2O_3 crystals formed in the RPR of the Al/ZnO$^{\langle 1-120 \rangle}$ couple after 20 min of interaction with aluminium at 1273 K

comparing the microstructures, it can be concluded that alumina is formed as the first layer and later the spinel layer grows at the expense of Al_2O_3.

Conclusions

For the first time, the effects of heating and cooling history on the interface transformation in highly reactive Al/ZnO system were dramatically reduced by combined application of two testing procedures allowing non-contact heating of a couple of materials as well as exposing of the interface at high temperature directly in the UHV chamber during the sessile drop wettability tests. Under conditions of this study, the liquid Al did not wet the ZnO substrate ($\theta > 90°$) independently from its crystallographic orientation.

Detailed characterization of exposed substrate-side interface formed between liquid Al and ZnO single crystals of different crystallographic orientations showed that non-wetting behaviour in highly reactive Al/ZnO system may be related with the formation of non-wettable reaction product since the α-Al_2O_3 phase, widely accepted to be wettable by liquid Al at 1273 K and expected in previous reports as a main reaction product in the Al/ZnO couple, was not found in this study. It was evidenced that the high-temperature interaction in Al/ZnO couple led to the creation of two reactively formed layers corresponding to the metastable Al_2O_3 and $ZnAl_2O_4$ spinel, both characterized with highly epitaxial growth. The thicknesses of those layers varied with respect to the drop content and time of interaction: longer time promoted the spinel growth at the expense of the alumina. The alumina was identified as either cubic γ-, tetragonal δ- or monoclinic λ-Al_2O_3.

Moreover, the type of created alumina was affected by the crystallographic orientation and chemistry of the top surface layer of the ZnO substrates showing dissimilar alumina formed even for the substrates of the same $\langle 0001 \rangle$ orientation but of various Zn- or O-terminated surfaces.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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