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TEM INVESTIGATION OF PHASES FORMED DURING ALUMINIUM WETTING OF MgO AT [100], [110] AND [111] ORIENTATIONS

ANALIZA FAZOWA METODĄ TEM PRODUKTÓW REAKCJI POWSTAŁYCH W CZASIE ZWILŻANIA PRZEZ ALUMINIUM PODŁOŻY MgO O ORIENTACJI [100], [110] I [111]

The interaction of liquid aluminium (5N) with single crystal MgO substrates of [100], [110] and [111] orientations (surface roughness <1 nm) were studied using sessile drop wettability test performed at 1000°C for 1 hour in vacuum (5×10^{-6} mbar). The observations performed using scanning electron microscopy (SEM) showed that the interaction of liquid metal with MgO crystals in all cases resulted in the formation of reaction products region (RPR) of thickness varying from ~40 up to ~80 microns in depth. In each case the RPR consisted mainly of coarse dendrite-like crystallites of few microns thick surrounded by net of much thinner channels. Occasionally away from the RPR centre the areas built of much finer but also dendrite- or filament-like crystallites were noted. The thin foils for transmission electron microscopy (TEM) investigations were cut using focused ion beam system (FIB) both from drop/RPR as well as RPR/MgO interfacial regions. The electron diffractions proved that the dominating coarse dendrite-like crystallites are of the same α -Al₂O₃ type throughout the whole RPR for all substrates orientations. Similarly, the colonies of finer crystallites always showed diffraction patterns characteristic for MgAl₂O₄ spinel. Therefore, the performed investigation indicated, that both the reaction layer depth and the reaction path represented by the sequence and type of phases present in Al/MgO RPR remain roughly similar for all examined orientations, i.e. that the substrate orientation control neither reaction kinetics, nor affects final phase composition of RPR.

Keywords: Al/MgO reaction, α -Al₂O₃, MgAl₂O₄, microstructure, TEM, EDS

Oddziaływanie ciekłego aluminium (5N) z mono-kryształicznymi podłożami o orientacji [100], [110] i [111] (chropowatość <1nm) badano metodą kropli leżącej w 1000°C przez 1 godzinę w dynamicznej próżni rzędu 10^{-4} Pa. Obserwacje z wykorzystaniem mikroskopii skaningowej (SEM) wykazały, że oddziaływanie ciekłego metalu z kryształami MgO we wszystkich przypadkach prowadziło do wytworzenia strefy produktów reakcji (tzw. reaction product region – RPR) o grubości od ~40 do ~80 μm . W strefach tych występowały wydzielania o kształcie dendrytycznym rozdzielone wąskimi kanałami aluminium. Na krawędziach strefy reakcyjnej stwierdzono obecność kolejnej strefy o grubości kilku- kilkunastu-mikrometrów wypełnionej materiałem o jeszcze drobniejszej włóknistej strukturze. Obserwacje mikrostruktury prowadzono z wykorzystaniem mikroskopii transmisyjnej na cienkich foliach wyciętych techniką FIB zarówno z granic obu stref, oraz z granicy RPR/MgO. Obserwacje te, w powiązaniu z analizą dyfrakcji elektronowych wykazały, że dla MgO wszystkich orientacji dominujące w RPR duże wydzielania o kształcie dendrytycznym odpowiadają fazie α -Al₂O₃. Równocześnie, analiza dyfrakcji drobniejszych krystalitów zlokalizowanych w pod-strefie ulokowanej na granicach poza centrum RPR wykazała, że mają one budowę charakterystyczną dla spinelu MgAl₂O₄. Przeprowadzone badania wykazały, że zarówno grubość RPR, a w tym jej pod-strefy drobniejszych wydzieleni na jej obrzeżach, jak też droga reakcji reprezentowana przez sekwencję i typ wydzielających się faz w czasie oddziaływania ciekłego aluminium jest identyczna dla wszystkich analizowanych monokryształicznych podłoży MgO, tj. orientacja tych podłoży nie ma wpływu ani na skład fazowy produktów reakcji ani też na kinetykę tego procesu.

1. Introduction

Ceramic moulds used in casting industry usually undergo fast degradation due to reaction of their walls with the liquid metal [1]. Aside of the damage inflicted on the moulds the reaction products may adversely affect the mechanical properties of the produced materials due to unwanted alloying or presence of non-metallic inclusions. One of the ways to circumvent these detrimental effects leads through a proper se-

lection of refractory materials used for mould production, i.e. trying to avoid the most reactive ones. It is relevant also in case of small additions applied as sintering aids in advanced structural ceramics.

The magnesia based containers used in every day foundry practice are especially strongly eroded by aluminium and its alloys. The investigations performed using sessile drop experiments at comparable conditions [2-6] confirmed that the Al – MgO system is indeed highly reactive producing thick reaction

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product region (RPR), despite the fact that such redox reaction is not favorable from the thermodynamic point of view. The Macevoy et al. [2] early measurements of a chemical composition of the RPR obtained using MgO of [100] orientation corresponded to that proper for the $\text{MgAl}_2\text{O}_4/\text{Al}(\text{Mg})$ composite. The more recent investigation by Shen et al. [5] relying both on similar microprobe measurements on substrates of [100], [110] and [111] orientations showed that the RPR is filled predominantly with $\text{Al}_2\text{O}_3/\text{Al}(\text{Mg})$ with only occasional presence of $\text{MgAl}_2\text{O}_4/\text{Al}(\text{Mg})$ areas. Our preliminary analysis performed with TEM of similar to their RPR formed on MgO substrate of [100] orientation also showed local presence of both of alumina and spinel [6]. The X-ray diffractometry performed by Shen et al. [5] not only confirmed the presence of MgAl_2O_4 spinel, but also helped to reveal several alumina phases, i.e. the $\alpha\text{-Al}_2\text{O}_3$ was noted for substrates of [100] orientations, but for two other orientations only phases including $\kappa\text{-}$, $\kappa'\text{-}$ and $\delta\text{-Al}_2\text{O}_3$ were detected. Therefore, the understanding of the reaction path at the Al/MgO interface needs more reliable description of the type and respective volume content of phases formed at RPR in Al/MgO samples.

The present experiment was aimed at analysis of the effect of the MgO substrate orientation on the phase content of the RPR using TEM method. The high spatial resolution of the latter allows a much more precise microstructure description than the X-ray diffractometry, even in case of as complex areas like those resulting from interaction of liquid aluminium and MgO substrates. The application of the relatively novel focused ion beam sample preparation technique, capable of producing thin foils from predetermined locations, are of special importance for such investigations.

2. Experimental

The sessile drop wettability tests with aluminium (5N) drop and single crystal MgO substrates of [100], [110] and [111] orientations were performed in vacuum not worse than 5×10^{-4} Pa at 1000°C for 1 hour. The wettability of MgO substrates was studied by the sessile drop technique and contact heating [7], using the experimental system described in Ref. [8]. The substrates obtained by arc melting before high temperature tests were cut to desired orientation and polished mechanically till surface roughness was < 1 nm.

The preliminary description of RPR was performed using scanning electron microscope equipped with back scattered electron (BSE) detector (E-SEM XL30, FEI). Next, the transmission electron microscopy (TECNAI SuperTWIN FEG 200kV, FEI) with the EDAX attachment for energy dispersive X-ray microanalysis was applied to obtain information both on its phase content as well as the chemical composition. The thin foils prepared using focused ion beam instrument (Quanta 3D, FEI) were cut from the Al drop/RPR and RPR/substrate boundaries.

3. Results

The aluminium drops placed on MgO of [100] and [110] orientations showed some instability during wetting

test, i.e. they tended to move to substrates sides and back. Only the one deposited on MgO of [111] orientation remain stable throughout the experiment. The examination of polished drop/substrate section using scanning electron microscopy method showed that in all three cases the interaction of liquid metal caused formation of a thick layer of RPR in the substrate (Fig. 1). In case of MgO of [111] orientation, RPR extends only slightly out of the drop on all sides (Fig. 1c), while in two other samples it took highly asymmetrical shape occasionally covering even substrate sides or bottom (Figs. 1a, b). Closer inspection of the investigated samples indicated that the respective RPR, especially those under the central part of the metallic drop, are of similar thickness varying from ~ 40 to ~ 80 microns (Fig. 2). They are all filled mostly with coarse

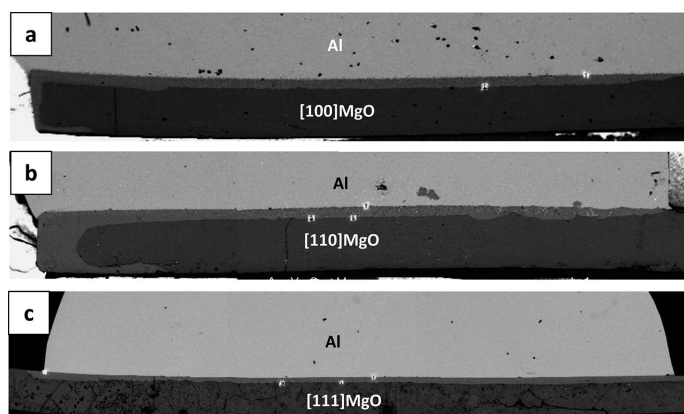


Fig. 1. SEM (BSE) images of sections through aluminium drop and MgO substrates at: a) [100], b) [110] and c) [111] orientations presenting characteristic shapes of RPR formed after wetting experiments

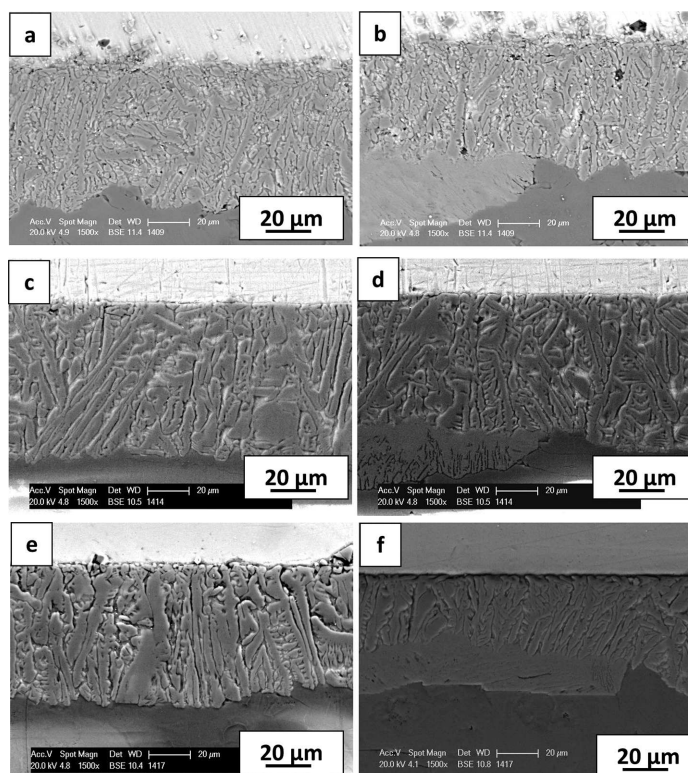


Fig. 2. SEM (BSE) images of the magnified section of RPR with coarse dendrite like crystallites formed between aluminium drop and MgO substrates at: a) [100], b) [110] and c) [111] orientations

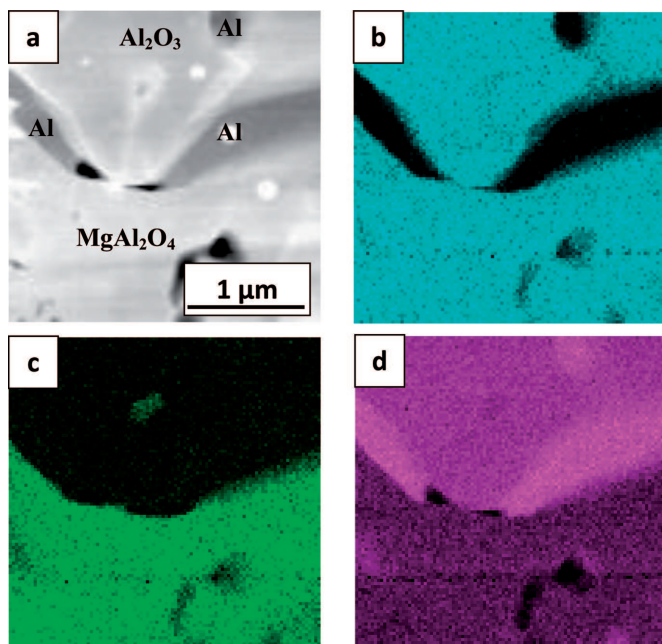


Fig. 3. STEM (HAADF) image of a boundary between coarse and fine dendrite-like crystallites formed in RPR in MgO substrate of [111] orientation (a) and accompanying maps showing distribution of oxygen (b), magnesium (c) and aluminum (d)

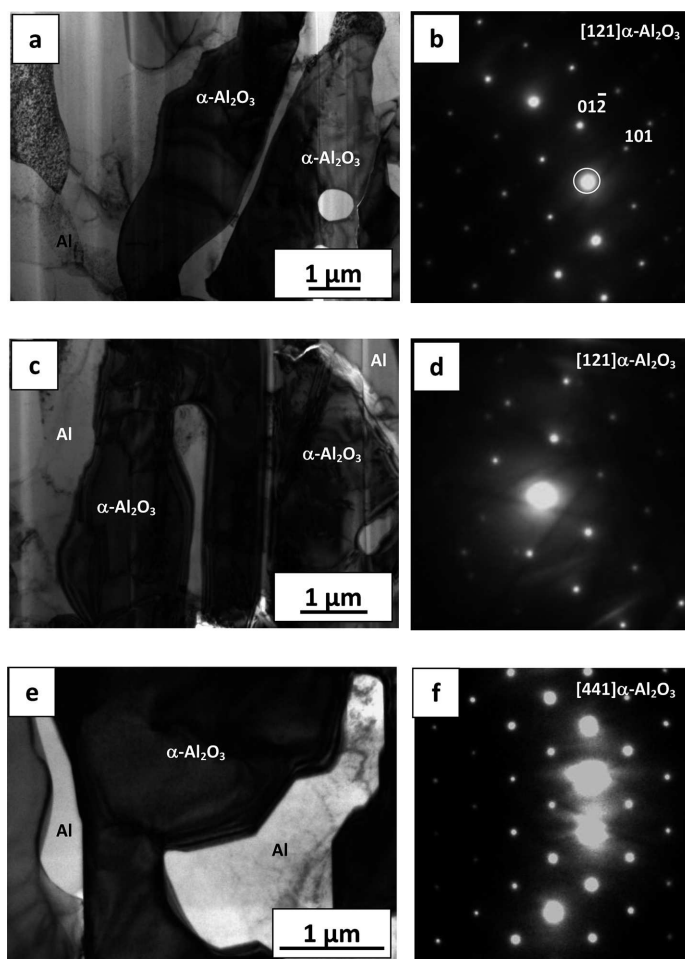


Fig. 4. TEM (BF) images of coarse dendrite-like crystallites with accompanying electron diffraction pattern formed in RPR in MgO of: a-b) [100], c-d) [110] and e-f) [111] substrate orientation

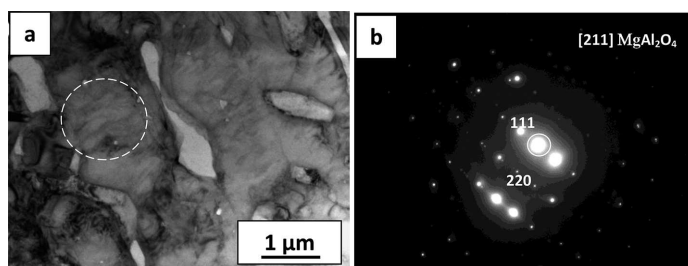


Fig. 5. TEM (BF) image of fine dendrite-like crystallites (a) with an accompanying electron diffraction pattern (b) formed in RPR in MgO of [111] substrate orientation

dendrite-like crystallites separated by much thinner channels extending from the aluminium drop (Fig. 2a,c,e). However, starting in the area furthest away from the centre (including substrate sides) and later penetrating in between the substrate and coarse dendrite-like crystallites a layers of much finer dendrite- or filament-like crystallites are formed (Fig. 2b, d, f). It is worth to note, that the areas of fine crystallites are formed in RPR of all samples including the one obtained from wetting of MgO of [111] orientation where they are present in the smallest volume.

The detailed examination of the RPR filled solely with coarse dendrite-like precipitates using scanning-transmission electron microscopy observations and X-ray energy dispersive microanalysis clearly indicated, that coarse dendrite-like crystallites built exclusively from aluminium and oxygen have to be some form of alumina separated by narrow channels filled with aluminium (Fig. 3). On the other hand the fine dendrite-like crystallites show presence not only of aluminium and oxygen, but also of magnesium indicating it as an MgAl_2O_4 spinel. The phase analysis taking into account α -, β -, γ -, κ -, κ' - and δ - Al_2O_3 and relying on selected area electron diffraction patterns like that in Fig. 4, gave a proper unique fit only with the former one. The thin foils were cut both from the area close to the metal drop and close to the MgO, i.e. covering the whole RPR area and therefore, basing on these results one may state that coarse crystallites independently of substrate orientations are built of a corundum type. Practically all α - Al_2O_3 crystallites were characterized by low defect density. Additionally, the neighboring ones were frequently of the same orientations (indicated by same diffraction contrast), as they were just the same “dendrite” branches sliced during focused ion beam cutting. The aluminium channels showed lot of dot defects originating from gallium ion implantation as well as some dislocations. The selected area electron diffraction also helped to confirm, that the finer dendrite-like crystallites located in colonies mostly away of the centre of the RPR were of the MgAl_2O_4 spinel type (Fig. 5b).

4. Discussion

The MgO mono-crystalline substrate orientations during the aluminium sessile drop wetting tests were first considered as one of more important parameter during such experiments [9]. It was suppose to influence - first of all - the reaction kinetic making itself visible trough changing thickness of reaction products layer formed at otherwise the same conditions including time, temperature, vacuum level and others. Next,

and to some extent connected with the above, a reaction path was supposed to be affected as well, i.e. the type and sequence of phases nucleated at the reaction front should be directly connected with substrate orientations.

However, the more recent papers, like those authored by Shen et al. [6] showed that at least the reaction layer depth remain roughly similar for all examined orientations. The approximately similar thickness of the RPR formed under the central part of the drop on all [100], [110] and [111] MgO substrates as showed present work (Fig. 1, Fig. 2a,c,e) fully confirmed the latter conclusions. The central part is most representative for the described process, as at sides the diffusion path for magnesium atoms up to liquid drop is much longer and of increasing length. The tendency of the metallic drops to shift its position while still in liquid form at [100] and [110] orientations resulting in asymmetrical shape of RPR away from it centre might be as well result of minor differences of surface finish, i.e. could also happen for the [111] orientation in case the experiments were repeated several times.

The reaction path represented by the sequence and type of phases present in Al/MgO RPR formed on substrate of different orientations remain dubious as well. All experiments reported up to date [2-5], as well as our own previous [6] and present results confirmed the presence of MgAl₂O₄ spinel phase, but always as a minor portion. Analyzing spectra acquired with XRD technique Shen et al. [5] stated that for [100] MgO substrate the RPR is predominantly filled with the α -Al₂O₃, while for [110] and [111] MgO other alumina phases like κ , κ' or δ do form. The phase analysis performed using electron diffraction in present work showed, that aside of spinel the RPR for all above substrate orientations contained only α -Al₂O₃. The one type of coarse dendrite-like crystallites found under the drop centre favors the latter standing, even as the phase analysis in case of alumina is with both technique neither easy as X-ray spectra are characterized by a numerous lines which intensity might vary with local texture nor decisive due to electron diffraction are acquired only from few crystallites.

5. Summary

The simultaneous application of range of analytical techniques including scanning and transmission electron microscopy backed by still novel FIB thin foil preparation technique allowed to precisely characterize the RPR formed during

Al/MgO sessile drop experiment performed using [100], [110] and [111] single crystal substrates.

The obtained results clearly indicate, that independently of the orientation of the substrates used during Al/MgO sessile drop wetting tests the thickness of resulting RPR is roughly similar and always filled predominantly with coarse dendrite-like α -Al₂O₃ crystallites, while at its sides as a minor portion presence of much finer MgAl₂O₄ spinel crystallites was regularly noted.

Summarizing, both the reaction layer depth and the reaction path represented by the sequence and type of phases present in Al/MgO RPR remain similar for all examined orientations, i.e. that the substrate orientation controls neither the kinetics of α -Al₂O₃ formation, nor affects final phase composition of RPR as MgAl₂O₄ spinel is always also present.

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