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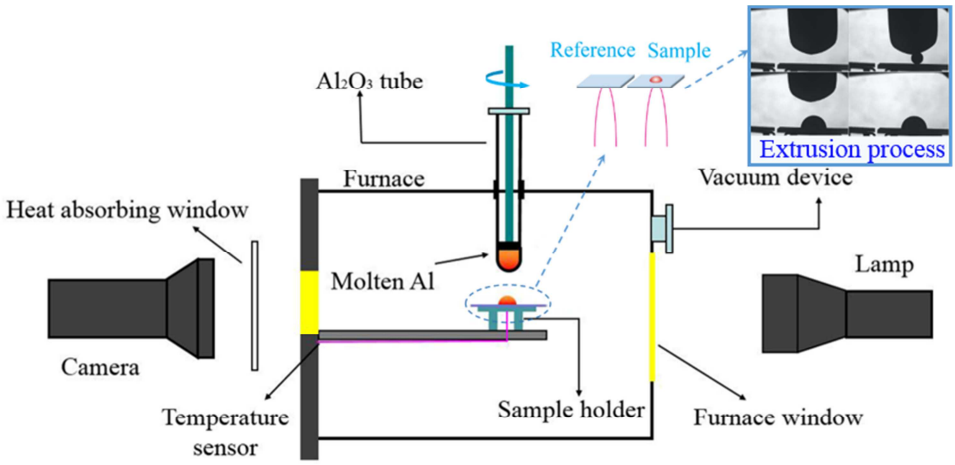

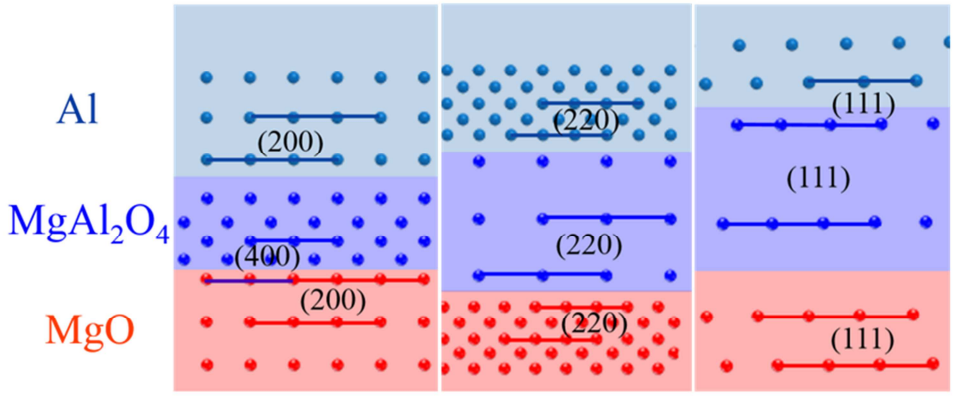

Heterogeneous nucleation of pure Al on MgO single crystal substrate accompanied by a $MgAl_2O_4$ buffer layer

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ABSTRACT

This paper investigates the correlations between interfacial reaction, crystallographic orientation relationship on the interface and the required undercooling for nucleation on different crystallographic planes of MgO. Thermal analysis and high resolution transmission electron microscopy were used to study the nucleation behavior of liquid, high-purity Al droplet on single crystal MgO substrates using a DSC with an integrated image capture system and a sessile drop apparatus. The results showed that the original substrate MgO would be completely replaced by the reaction product $MgAl_2O_4$ at the interface owing to the chemical reaction between liquid Al and the MgO substrates. In addition, the same crystal structure with the original MgO substrate is achieved in the new $MgAl_2O_4$ layer. The orientation relationship between $MgAl_2O_4$ and Al is consistent with the theoretical prediction according to the Bramfitt's lattice misfit theory and Edge-to-Edge model. Consequently, the generated $MgAl_2O_4$ significantly influences the detected undercooling.

Keyword

Heterogeneous nucleation; Orientation relationship; Nucleation undercooling; Soldification.

1. Introduction

Adding an effective nucleating substrate to liquid metal, known as inoculation, is a common practice to achieve significant grain refinement of castings and ingots. Nucleation theory identifies the importance of heterogeneous substrates as a mechanism for reducing the free energy barrier to nucleation [1]. Revealing the mechanisms of heterogeneous nucleation of a liquid metal on an effective substrate is not only of great scientific interest but also of technological importance [2]. Therefore,

the study of heterogeneous nucleation has been an important topic in the metal solidification field for decades, attracting numerous researchers using various techniques and materials to meet industrial requirements and for alloy chemistry. In general, the nucleating potency of a heterogeneous substrate can be attributed to structure mismatch and orientation between solid to be nucleated and substrate, material chemistry including interaction and segregation to the interface, and temperature such as undercooling. Theoretically, a number of factors affecting the nucleation potency include ~~the effect of~~ the size and ~~size~~ distribution of the nucleating particles [3, 4], the surface roughness of a substrate [5], the cavity geometry of substrates [6], the structure and composition of the nucleating surface [7], and the chemical reaction between the liquid metal and substrates [8].

In a study on nucleation catalysis in supercooled liquid tin, Sundquist [9] postulated that the nucleus is a layer of atoms adsorbed on the flat substrate when liquid tin nucleates with a low undercooling, and the adsorbed layer can be arranged as a nucleation embryo in the liquid. Oh et al. confirmed that an in-plane, ordered pure Al atomic layer exists at the liquid Al/solid Al_2O_3 interface through experimental investigation [10]. The latest experimental and theoretical studies all suggest that the adsorbed layer formed at the liquid/substrate interface is a general phenomenon for a nucleation interface and may impose important effects on nucleation [11]. The adsorption layer can be described as a solid-like precursor, and the lattice mismatching between the precursor and substrates then becomes the major energy barrier for the nucleation of liquid. It means that the lattice misfit between substrates and precursor becomes essential to determine if nucleation will occur [12-14]. Much of the research involving Al_3Ti/TiB_2 suggests that the interface composition and structure are the key points to improving the potency of nucleation [4, 15]. Recently, Wang et al. [11] and Li et al. [16] studied the segregation of Cu at the interface between the Al_2O_3 substrate and the Al-Cu alloy. The solute element, in this case Cu, can modify the lattice matching of the nucleation interface, and the preferred crystal orientation was affected by the substrate structure. Based on the lattice misfit effect on heterogeneous nucleation, Wang et al. have carried out a series of experiments with varied lattice misfits by changing the Al_2O_3 crystal plane of the substrate and formulating the experimentally measured undercooling with corresponding lattice misfits [17] and proposed an integrated model to predict the nucleation undercooling. Experimental studies by Perepezko's team [18-20] and computer simulations [21] have all indicated that the orientation relationship and lattice mismatch between substrate and nucleus are important factors that influence the potency of the substrate and the undercooling required for nucleation. The better the lattice matching is, the higher the nucleation potency. Minimization of strain energy at the interfacial boundaries between the two phases requires good atomic matching. Brown et al. [22] observed in situ the orientation relationship of the interface plane between the substrate and nucleus, and also revealed it would affect the potency of the substrate and the required undercooling for nucleation.

MgO and $MgAl_2O_4$ are believed to be effective heterogeneous nucleating agents for Al based alloys due to their similar lattice structures and small lattice misfits [23, 24]. However, most information on the interaction of molten aluminum with MgO was, until now, gathered through wetting experiments, within temperature ranges up to 1137°C. Fujii et al. [25] identified the presence of Al_2O_3 at the interface between the MgO and liquid Al. McEvoy et al. [26] reported that the reaction product of molten Al with MgO was $MgAl_2O_4$. Morgile et al. [27] clarified that the $MgAl_2O_4$ was an intermediate product and that Al_2O_3 was a final product of the reaction. It should be noted here that most researchers [8, 23, 25-28] reported that interfacial reaction between molten Al and MgO substrates occurred at a much higher temperature than the normal casting temperature between 700-800°C. Zhang et al. [8] have investigated the nucleation mechanism of Al nuclei on MgO at the experimental temperature of 1027°C, and found that the nucleation behavior is more complicated due to the varied chemical reaction at this high temperature. Nevertheless, less attention has been paid to the nucleation behavior of pure Al melt on MgO substrate and the generated reaction products at the normal casting temperature. In addition, no literature has been reported with respect to the formation of a perfect crystal and the orientation relationship between the MgO crystal and reaction products.

In this work we utilized thermal analysis and high resolution transmission electron microscopy to study the nucleation behavior of molten Al on single crystal MgO substrates, using a differential scanning calorimeter (DSC) incorporating an image capture system and a sessile drop system. The aim of this paper was to clarify the reaction product and the corresponding orientation relationships at the interface of Al/MgO heated to a maximum temperature of 750°C, and present the resulted undercooling to understand the heterogeneous nucleation of molten Al on single crystal MgO.

2. Experimental apparatus and procedure

As illustrated in Fig 1, a modified DSC measurement apparatus (Thermal Analysis Company, Selb Germany) has been used to investigate heterogeneous nucleation, with the apparatus consisting of four parts: furnace, image acquisition system, extrusion device, and evacuating system with a rotary pump and a turbo molecular pump.

MgO and $MgAl_2O_4$ single crystals with dimensions of $14\times10\times0.5$ mm^3, used as substrates in this study were purchased from Shanghai Hengda Optics and Fine Mechanics Co., Ltd. These single crystals were polished to an average roughness (Ra) of less than 1 nm using a nano-diamond slurry. Ultrahigh purity aluminum (99.9995%) was employed as the solid to be nucleated in experimentation. Prior to the DSC experiment, both the substrate and Al specimen were immersed in acetone and ultrasonically cleaned, then the substrate was placed horizontally on the temperature sensor while the Al specimen was placed in a high purity alumina tube with a 1 mm

diameter hole in the bottom.

The furnace was first evacuated to 5×10^{-5} Pa, and then heated to the designed temperature of 750°C in a vacuum with a heating rate of 15°C/min. The alumina tube can be evacuated through the hole at the bottom keep the same atmosphere with the furnace. The chamber was filled with high purity argon with oxygen content less than 0.1 ppm, and then molten Al was extruded through a hole at the bottom of the alumina tube and dropped onto a single crystal substrate to keep 3 mins at temperature of 750°C before cooling. In this way, the initial oxide on the Al surface was mechanically removed as the liquid passed through the hole. In the current experimental set up, the hemispherical droplet sample was kept at about 1.5 mm in diameter. The sample was cooled at a rate of 15°C/min. After cooling down to room temperature, the Al sample with the substrate was removed from the chamber. The temperature was recorded by a platinum-rhodium-platinum thermocouple with an accuracy of ±0.1°C. The experiments were repeated four times to ensure the repeatability of the experiments and the reliability of the results.

The crystal structure of solidified samples at the interface was characterized using high-resolution transmission electron microscopy (HRTEM) technique. Thin cross-sectional foil samples for HRTEM observation were prepared according to standard metallographic practice, and then milled by focused ion beam (FIB) using a FEI 600i dual-beam system under the condition of 30kV. Conventional TEM and HRTEM analyses were conducted using a JEM-2100F microscope operated at an accelerating voltage of 200kV.

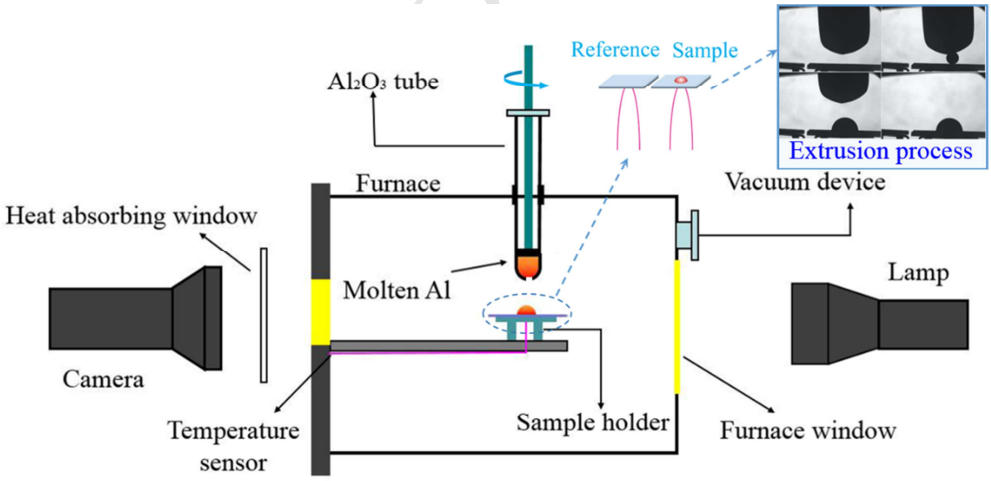

Fig.1 Schematic illustration of the improved DSC measurement

3. Results

3.1 Nucleation undercooling

Fig. 2 presents measured DSC curves at the cooling rate of 15°C/min for the liquid Al solidified on the different MgO substrates with (100), (110) and (111) crystal planes. In this study, the undercooling is defined as the temperature difference between the equilibrium melting temperature (660.3°C) and the nominal start of solidification

temperature T_s. As shown in Fig. 2, the value of T_s achieved in the twelve DSC experiments are varied between 652.7 and 656.9°C. In addition, the variation of T_s can be observed even if the DSC measurements were repeatedly performed by using the substrate with the same crystal plane. Fig.2 also shows the corresponding undercooling ($\Delta T = 660.3 - T_s$) of Al on MgO substrates with the three different crystal planes. The fluctuation of undercooling, varied from 3.4°C to 7.5°C, can be found in these twelve DSC experiments of Al/MgO. Moreover, since the fluctuation range is almost the same by comparing the achieved undercooling of Al solidified on MgO substrates with different crystal planes, it indicates that the undercooling is not influenced by the crystal planes of the MgO substrate.

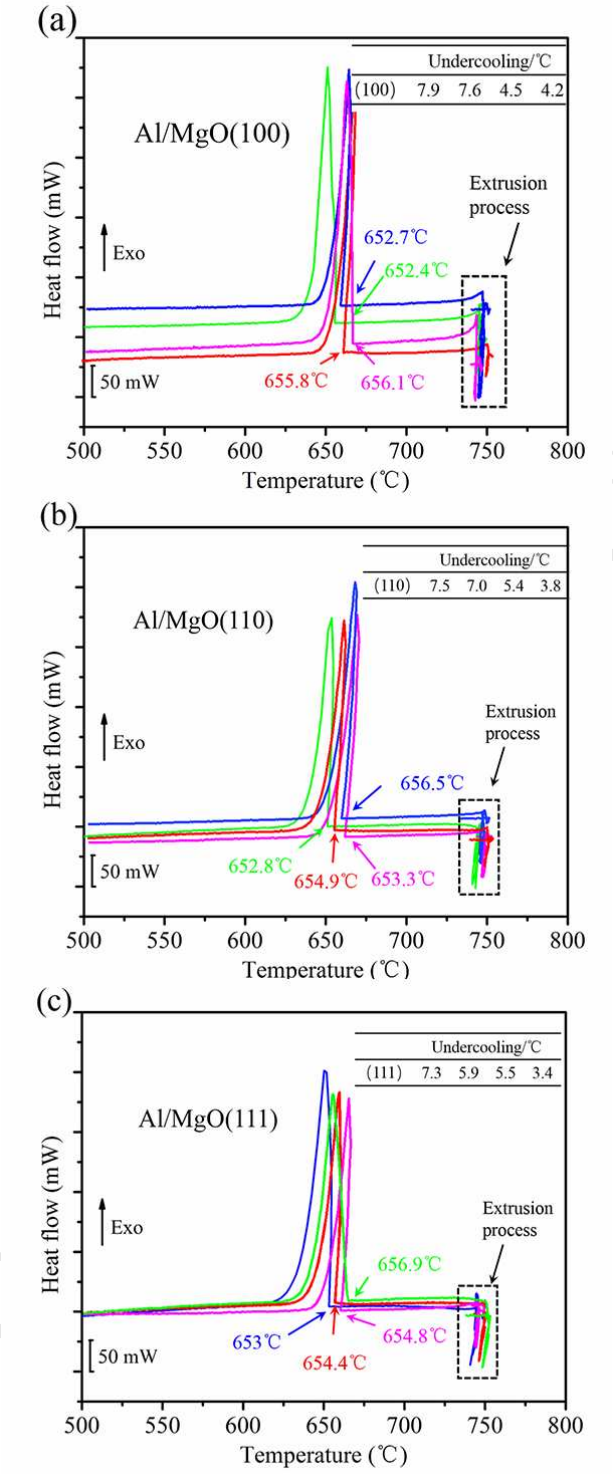

Fig.2 DSC solidification exotherms of Al droplet on MgO substrate with different lattice planes of (a) (100), (b) (110) and (c) (111) at the cooling rate of 15℃/min (The curves with 4 different colours means that the DSC experiments are repeated four times with different samples).

3.2 Characterization of Al/MgO interfaces

In order to further investigate the crystallographic orientation and variation of nucleation behavior, samples solidified on (100), (110) and (111) planes of MgO substrates were examined using TEM and HRTEM. Fig. 3 (a-f) shows the TEM images and EDS on the interfaces between the new crystal and MgO substrates. It can be observed that these interfaces are straight and distinct, and intermediate layers with distinct image contrast can be distinguished between the aluminum and MgO substrate. The thickness of the intermediate layer is between 10 and 40 nm. In addition, the intermediate layer in Fig. 3(b) and (f) is continuous and straight, which differs from the small islands and local formations in Fig. 3(d). With TEM-EDS analysis, it was confirmed that the upper right area corresponds to Al phase, while the lower left is the MgO substrate. The EDS mapping clearly shows that the distribution of the Mg, O and Al elements is similar in the intermediate layers of these three samples respectively solidified on MgO substrates of (100), (110) and (111) planes. It indicates that the generated intermediate layers, composed of aluminum, oxygen and magnesium, may be the same phase in these three samples. ~~Aside from this layer, the Al and MgO substrates were also presented.~~

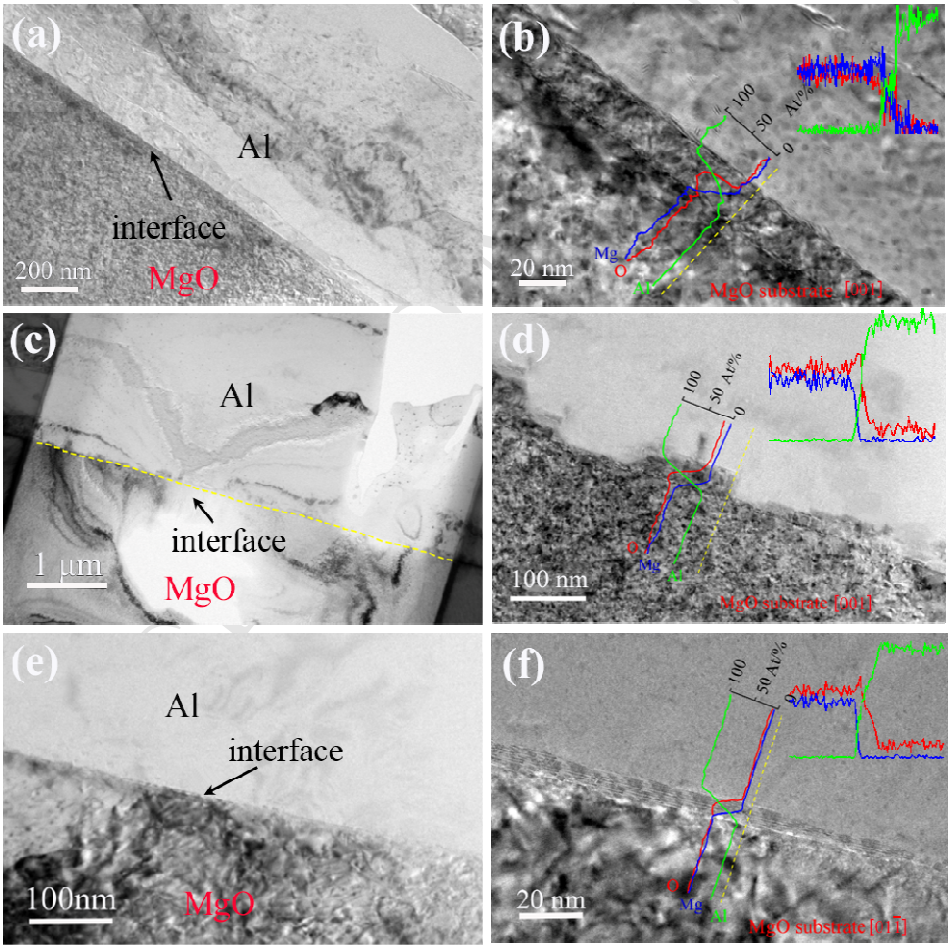

Fig.3 TEM images of (a) Al/(100)MgO, (c) (110)MgO, (e) (111)MgO nucleation interface take along MgO [001],[001] and [01$\bar{1}$], separately. And corresponding EDS of (b),(d),(f), and the accompanying lines showing distribution of oxygen, magnesium and aluminum.

To further investigate the phase composition and structure of the nucleation surface,

196 samples solidified on (100), (110) and (111) planes were examined using HRTEM.
197
198 **Al/MgO (100) interface.** The HRTEM image of cross sections of the Al/MgO (100)
199 interface are shown in Fig. 4. The formed intermediate layer completely takes up the
200 interface of MgO, which means that it would act as a new nucleation substrate. Fig.
201 4(b) and (c) show a magnified HRTEM image of the interface viewed along the [001]
202 zone axis of the MgO substrate. Well-defined atomic rows and lattice planes can be
203 identified. Fast Fourier transformation (FFT) analysis indicates that the intermediate
204 layer is a face-centered cubic (FCC) structure with the spacing of 0.201-0.204 nm and
205 0.279 nm, which corresponds to the spacing of $MgAl_2O_4$ (400) and (220), respectively.
206 Since both the crystal structure and lattice spacing are consistent with that of
207 $MgAl_2O_4$ (FCC, a=0.804 nm) rather than α-Al_2O_3 with the hexagonal close packed
208 (HCP) structure and lattice spacing of a=0.475 nm and c=1.297nm, it means that the
209 phase of the intermediate layer is only composed of $MgAl_2O_4$. Moreover, as shown in
210 Fig. 4(c), it can be found that the (400) plane of $MgAl_2O_4$ is perfectly parallel to the
211 (200) plane of the interface of the MgO substrate because the lattice arrangement of
212 (400) is identical to that of (200). The lattice arrangement of Al and the new phase
213 $MgAl_2O_4$ is clearly observed in Fig.4(b). Using FFT analysis, it was found that the
214 (200) planes of Al have a d-spacing of 0.200 nm and are parallel to the (400) planes of
215 the $MgAl_2O_4$ phase with a d-spacing of 0.201 nm. According to the presented lattice
216 plane shown in Fig. 4, the orientation relationship can be summed up as [001] (400)
217 $MgAl_2O_4$// [001] (200) MgO and [001] (220) $MgAl_2O_4$// [001] (220) Al.

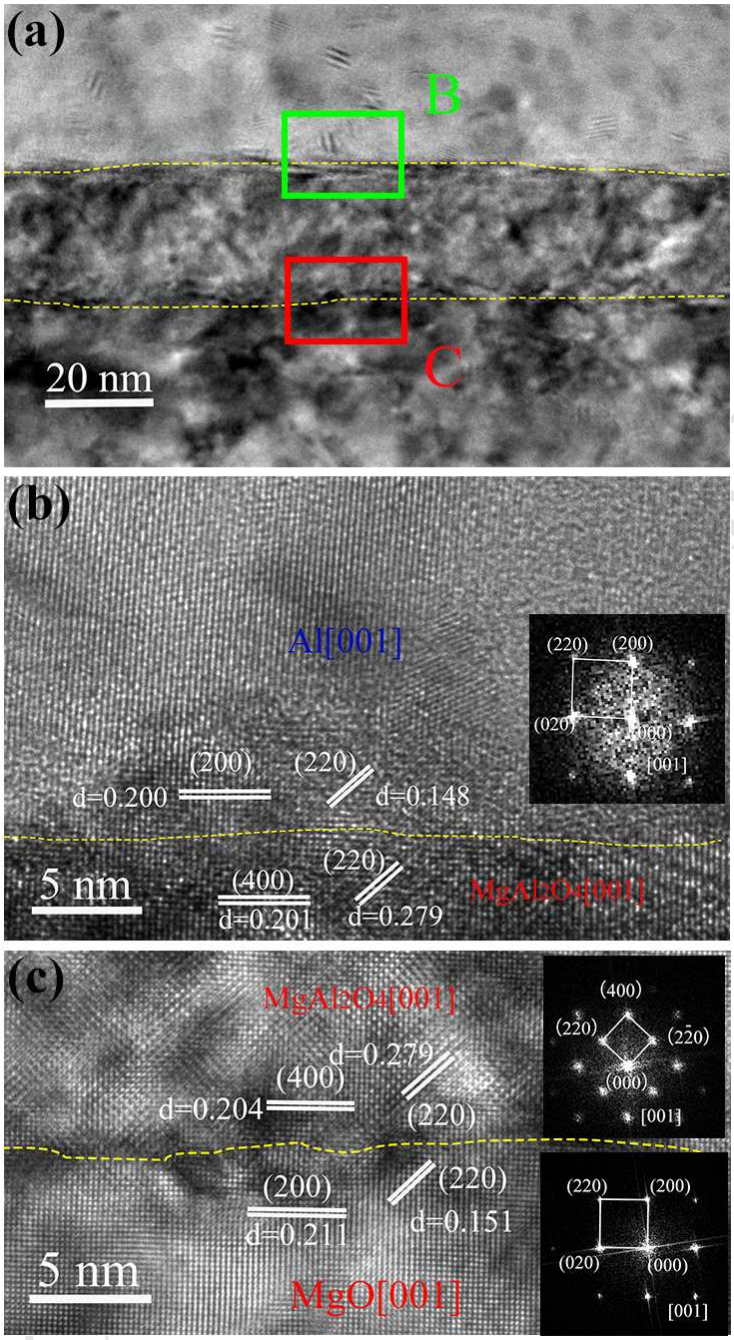

Fig.4 HRTEM image of Al/MgO(100) taken along [001] MgO zone direction (a); image of HRTEM of Al/$MgAl_2O_4$ interface,which corresponds to frame (B) of (a), and the FFT image of HRTEM (b); image of HRTEM of $MgAl_2O_4$/MgO interface, corresponding to frame (C) of (a), and the FFT image of HRTEM (c)

Al/MgO (110) interface. Fig. 5 is the HRTEM image of the sample solidified on the MgO (110) plane, with the Al crystal being viewed along its [001] zone axis. The interface of Al, intermediate layer and MgO were clearly seen in the Fig. 5(a), respectively, which are marked with yellow dashed lines. Fig. 5(b) and (c) display a magnifying HRTEM image of the interface, which was of selected area in Fig. 5(a). Through FFT analysis of the HRTEM, the interplanar crystal spacing of the MgO substrate was 0.148 nm and 0.216 nm, and they respectively correspond to the planes of (220) and (200). It is worth noting that the lattice structure of MgO (220) is

identical to that of (110), therefore, the (110) plane of MgO is parallel to the interface. Meanwhile, the intermediate layer is a FCC structure with d-spacing of 0.203 and 0.276 nm respectively corresponding to the (400) and (220) planes, which suggests that the intermediate layer is also $MgAl_2O_4$. In addition, it was also noted that the (220) and (200) planes of MgO are perfectly parallel to the (220) and (400) planes of $MgAl_2O_4$, while being parallel to the (220) and (200) Al planes. In other words, the orientation relationship among them is (220) $[001]_{Al}$ // (220) $[001]_{MgAl2O4}$ // (220) $[001]_{MgO}$, and (200) $[001]_{Al}$ // (400) $[001]_{MgAl2O4}$ // (200) $[001]_{MgO}$.

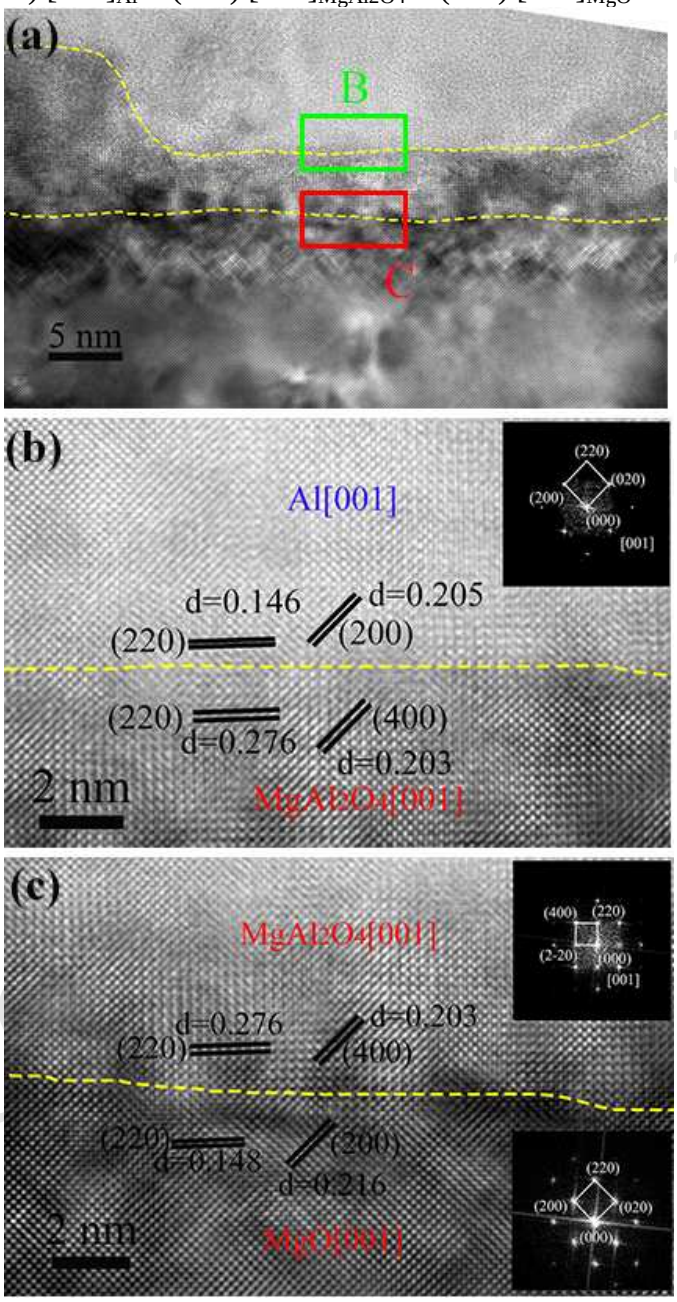

Fig.5 HRTEM image of Al/MgO(110) take along [001] MgO zone direction and the FFT image of HRTEM(a); image of HRTEM of Al/$MgAl_2O_4$ interface, which corresponds to frame (B) of (a), and the FFT image of HRTEM (b); image of HRTEM of $MgAl_2O_4$/MgO interface, corresponding to frame (C) of (a), and the FFT image of HRTEM (c)

Al/MgO (111) interface. A similar analysis method was adopted to observe the interface in Al/MgO (111) with the incident electron beam being parallel to the [01$\bar{1}$] axis of MgO, as shown in Fig. 6. The interface was marked with a yellow dashed line. The FFT image is shown in Fig. 6 by taking a Fourier transform of the HRTEM. The FFTs correspond to Al, $MgAl_2O_4$ and MgO, separately. The interplanar spacing in the middle area was consistent with a FCC structure with spacing of 0.473 nm for the (111) lattice plane. Since the crystal structure and the corresponding spacing shown in the middle area is also the same as that of $MgAl_2O_4$, it means that the produced intermediate layer is still $MgAl_2O_4$ as already found in Al/MgO (100) and (110). Moreover, TEM examination confirmed that the reaction product $MgAl_2O_4$ displays the (111) plane as the natural surface. It can be seen that the (111) plane of $MgAl_2O_4$ is parallel to the (111) plane of MgO and Al as well as the interface, as shown in Fig.6. The orientation relationship was thus established as $(111)_{Al}$ // $(111)_{MgAl2O4}$ //$(111)_{MgO}$.

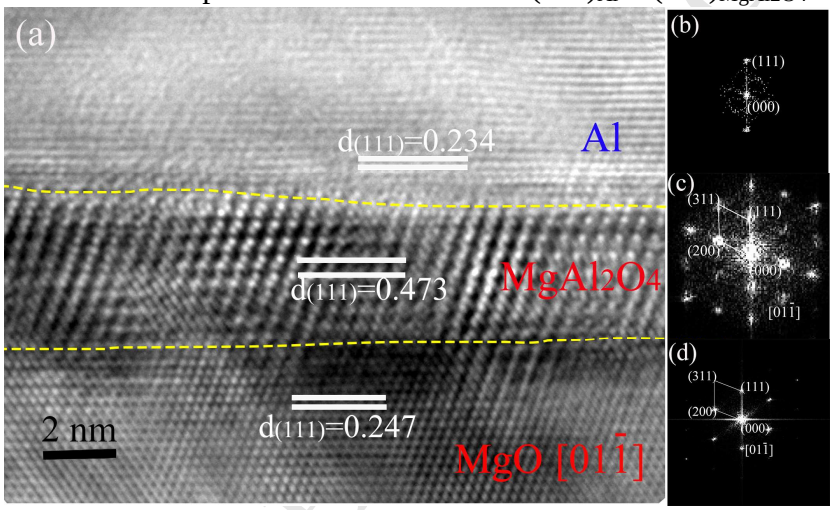

Fig.6 HRTEM image of Al/MgO(111) take along [01$\bar{1}$] MgO zone direction(a) and the FFT images of HRTEM(b),(c) and (d)

4. Discussion

4.1 Formation of $MgAl_2O_4$ on the Al/MgO interfaces

A number of researchers have investigated the interfacial reaction on the Al/MgO system [8, 23, 26-29]. Zhang et al [8] reported the reaction products of Al_2O_3 and $MgAl_2O_4$ between liquid Al and MgO at the temperature of 1027°C for 30 s, and similar reaction products formed on the interface were also found by Morgiel et al [27]. However, when investigating the wetting of molten Al on the MgO substrate in the temperature range of 1000°C to 1200°C, Shen et al [29] found that more complex interfacial reactions produced different phases of Al_2O_3 on Al/MgO systems, with no $MgAl_2O_4$ being detected. In their study, the final reaction products have been identified as primarily α-Al_2O_3 phase for (100) MgO and κ'-, κ- and δ-Al_2O_3 phases for (110) and (111) MgO, without a pronounced $MgAl_2O_4$ phase [29]. McEvoy et al [26] investigated the Mg concentration profile in a section of $MgAl_2O_4$ formed through interfacial reaction between molten Al and MgO. Their experimental results

revealed that the reactions between Al and MgO substrate are sensitive to the substrate orientation. Since the oxygen framework in MgO is quite similar to that in $MgAl_2O_4$, the layer may be supposed to grow epitaxially by diffusion of Al or Mg metals through a relatively unchanged oxygen lattice[26]. However, our experimental results demonstrate that only the $MgAl_2O_4$ phase is produced as a new substrate to connect the Al and MgO regardless of the substrate orientation when the Al melt was cooled from 750°C.

After the molten aluminum was dropped on the substrates in the present study, the following chemical reaction[27, 30] may take place:

$$2[Al] + 4MgO = MgAl_2O_4 \text{ (nucleated on MgO)} + 3[Mg] \quad (1)$$

The brackets indicate that the elements were in liquid state. In reality, the reaction direction is dependent on the change of the Gibbs free energy for the reaction ΔG_r. If ΔG_r is negative, the direct reaction could take place. Otherwise, the reverse reaction would occur. According to Equation (1), the changes in the Gibbs free energy for the reaction can be described as:

$$\Delta G_r = \Delta G_f^o(MgAl_2O_4) - 4\Delta G_f^o(MgO) + RT\ln\left(\alpha_{Mg}^3 \Big/ \alpha_{Al}^2\right) \quad (2)$$

where ΔG_f^o(i) is the standard Gibbs free energy change of formation (J/mol), R is the gas constant (J/(mol·K)), T is the absolute temperature (K) and α_j is the activity of component j in the solution. The thermodynamic conditions of the reaction of MgO, $MgAl_2O_4$ and Al were also discussed by Shi et al [30] in detail. Using Equation (2) and corresponding thermodynamic data from the literature [30], we calculated the change in the Gibbs free energy for the reaction at the temperature of 750^{o}C and 660 ^{o}C is estimated as -44.4 kJ/mol and -7.4 kJ/mol, respectively. It means that the reaction time between the molten Al and MgO substrate is about 9 mins.

According to the DSC curves shown in Fig. 2, the peak for the chemical reaction is not observed, which means the influence of chemical reaction heat on the undercooling should be ignored. As mentioned, the thickness of the $MgAl_2O_4$ is on the nanometer scale, indicating that the reaction was not significant under our experimental conditions with a lower temperature and a shorter period of time for this reaction in comparison with previous research performed at 1023°C [24]. Another phenomenon found in this study is that the thickness of the produced $MgAl_2O_4$ is between 20-40nm as shown in Fig.3, which is far less than the thickness of the produced intermediated layer in Al/MgO shown in the previous research [8]. It may be due to the higher temperature and longer time that were employed to sufficiently provoke the interfacial reaction in the previous studies. ~~Therefore, it is reasonable to conclude that the temperature and reaction time can significantly influence the formation of a newly produced layer.~~

4.2 Orientation relationship induced by heterogeneous crystal

In our studies, the HRTEM images of $MgO/MgAl_2O_4/Al$ regions show that there is a specific orientation relationship among the MgO substrate, reaction product $MgAl_2O_4$ and Al. Orientation relationships were found to be of the kind shown in Fig. 7, namely

$$(100)_{MgO}//(100)_{MgAl2O4}//(100)_{Al},\ [001]_{MgO}//[001]_{MgAl2O4}//[001]_{Al};$$

$$(110)_{MgO}//(110)_{MgAl2O4}//(110)_{Al},\ [001]_{MgO}//[001]_{MgAl2O4}//[001]_{Al};$$

$$(111)_{MgO}//(111)_{MgAl2O4}//(111)_{Al},\ [01\bar{1}]_{MgO}//[01\bar{1}]_{MgAl2O4}.$$

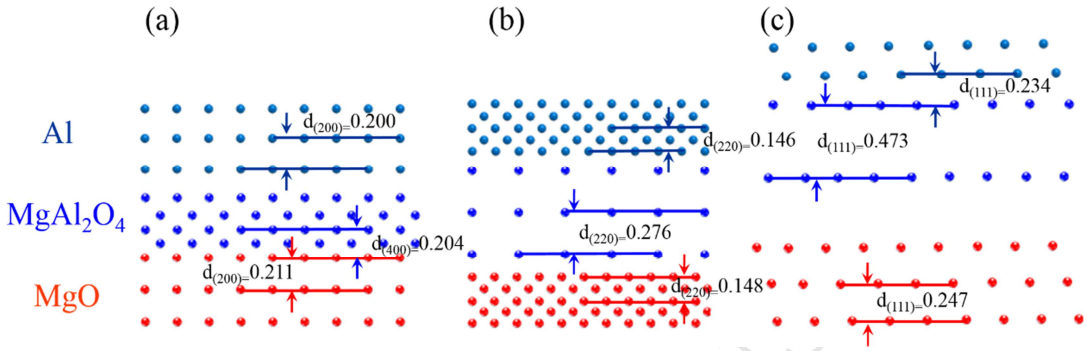

Fig.7 Schematic illustration of interface matching for Al on (a) (100), (b) (110) and (c) (111) planes of MgO substrate.

The interfacial free energy at the nucleating interface is the dominating factor in heterogeneous nucleation from a thermodynamic point of view. However, it is determined by chemical reaction, interface structure, wettability etc. Therefore, a simple description of this energy is difficult [23, 31, 32]. In practice, nucleating potency can be assessed by comparisons of the perfectness of the lattice matching. A smaller lattice misfit means a low lattice strain energy between two phases, and therefore a smaller undercooling required for nucleation [33]. A favored orientation relationship always corresponds to a low interfacial energy and a relatively stable mode thermodynamically [34].

A theoretical approach to assess the nucleating potency is to calculate the lattice misfit at the interface between the substrate and matrix. According to Bramfitt's two-dimensional misfit theory [31] and the detected plane of a new crystal with the substrate (see Fig. 7), we figured out that the lattice misfit for $Al(200)/MgAl_2O_4(400)$, $Al(220)/MgAl_2O_4(220)$ and $Al(111)/MgAl_2O_4(111)$ are all 1.17% in Al/MgO system. Here, the lattice misfit was calculated based on the coefficients of thermal expansion at the equilibrium melting point of pure Al of 660℃[35, 36]. It should be noted that the planes in this work are exactly the low index planes as stated in Bramfitt's model, which is consistent with the obtained misfit values from HRTEM.

Moreover, the edge-to-edge model [12, 13, 37-40] was used to verify the orientation relationship between two components based on the actual crystal structures and the corresponding atom positions. The model is based on the matching of rows of atoms and habit plane across the interface. Al, MgO and $MgAl_2O_4$ have the same FCC structure with a lattice parameter of 0.4046nm, 0.4200nm and 0.8080nm, respectively.

Table 1 shows the space group, SG number and other parameters. As discussed in the literature [34], they have the same close packed directions and planes, and accordingly, the derived packed directions are [100], [110] and [111], while the planes are (100), (110) and (111) respectively.

As reported in the literature [12], the interatomic spacing misfit along the matching directions and the interplanar spacing misfit of matching planes were required to be less than 10% and 6%, respectively. Due to the interface reaction, the $MgAl_2O_4$ would take up the original interface of Al and MgO. Hence, the probable orientation relationship between Al and $MgAl_2O_4$ was calculated, with the result shown in Table 2. It can be seen that there are three possible matching pairs, which are [100] Al//[100]$MgAl_2O_4$, [110]Al//[110]$MgAl_2O_4$, where the interatomic spacing misfits are all 0.16%. In the same way, the possible matching planes are (200) Al//(200) $MgAl_2O_4$, (220) Al//(220) $MgAl_2O_4$ and (111) Al//(111) $MgAl_2O_4$, which were calculated to be 0.16%. According to the edge-to-edge matching model, the matching directions should belong to the matching planes. Hence, the orientation relationship between Al and the MgO substrate could be predicted: (200)Al//(200)$MgAl_2O_4$, [001]Al//[001]$MgAl_2O_4$ or [011]Al//[011]$MgAl_2O_4$; (220)Al//(220)$MgAl_2O_4$, [001]Al//[001]$MgAl_2O_4$ or [1 $\bar{1}$ 0]Al//[1 $\bar{1}$ 0]$MgAl_2O_4$; (111)Al//(111)$MgAl_2O_4$, [1$\bar{1}$0]Al//[1$\bar{1}$0]$MgAl_2O_4$, which can be confirmed by our experiment results.

Table 1. The space group, SG number, crystal system, lattice parameter and atom position of Al and MgO

Compound	Space group	SG number	Crystal system	Lattice parameter	Atom position
Al	Fm-3m	225	Cubic	0.4046	0.5,0.5,0
MgO	Fm-3m	225	Cubic	0.4200	Mg:0,0,0 O:0.5,0.5,0.5
$MgAl_2O_4$	Fd-3m	227	Cubic	0.8080	Mg:0.5,0.5,0.5 Al:0.125,0.125,0.125 O:0.264,0.264,0.264

Table 2. Interatomic and Interplanar spacing misfit of possible matching directions and planes between Al and MgO

Al/$MgAl_2O_4$	f_1			Al/$MgAl_2O_4$	f_2		
	[100]	[110]	[111]		(200)	(220)	(111)
[100]	0.16	29.40	13.54	(200)	0.16	29.4	15.28
[110]	29.40	0.16	22.28	(220)	5.87	0.16	8.69
[111]	18.48	15.28	29.40	(111)	13.54	22.28	0.16

Note: f_1 is the interatomic spacing misfit of the close packed directions; f_2 is the interplanar spacing misfit of close packed planes

4.3 Undercooling of molten Al nucleated on MgO substrate

Undercooling of 22-28°C and multi nucleation interfaces in Al/MgO were reported in the literature [8]. However, the undercooling of Al solidified on MgO substrate achieved in the present study is only between 3 to 8°C. It is mostly likely due to the significantly different measurement methods and experimental conditions between the current study and that employed in the literature [8, 11, 16]. Our experimental results have shown that the intermediate layer is only composed of $MgAl_2O_4$ phase, which is the new substrate for the nucleation of Al melt. In addition, the crystal orientation of newly produced $MgAl_2O_4$ phase is driven by the orientation of the original MgO substrate, and the perfect orientation matching between the produced $MgAl_2O_4$ and the original MgO are observed. Hence, in order to further confirm the undercooling of Al/MgO achieved in our study, DSC experiments of molten Al solidified on $MgAl_2O_4$ (110) and (111) were performed and the corresponding undercooling is shown in Fig.8. It can be noted that the undercooling of the Al/$MgAl_2O_4$ system is very close to that of Al/MgO. This further confirms that the newly formed $MgAl_2O_4$ acted as the nucleation surface, and the initially terminated planes of the MgO substrates were isolated by the $MgAl_2O_4$.

The variation of undercooling for each Al/MgO(100), (110), (111) may be due to the essential feature of heterogeneous nucleation. According to the classical nucleation theory, there is a critical radius for the occurrence of nucleation. In practice, the structure or energy fluctuation is necessary to support the embryos whose size is closed to the critical size to trigger nucleation. It should be noted here that the size of embryos close to the critical size is not a point but a size range, which will lead to the nucleation temperature varied in a corresponding range as well as the variation of undercooling.

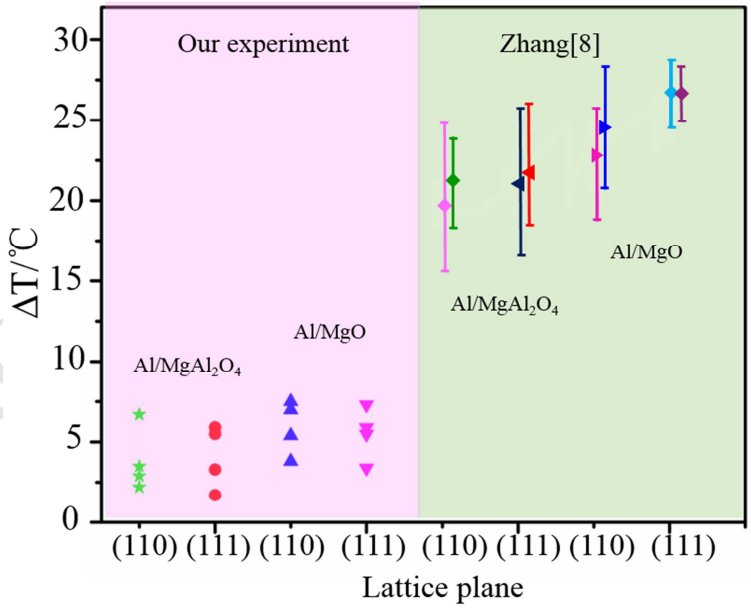

Fig.8 Undercooling of Al on $MgAl_2O_4$, and MgO substrates with different lattice planes. In contrast, the experimental undercooling includes the other data for liquid Al nucleated on the same substrates from literature [8].

In this study, a new and single substrate $MgAl_2O_4$ was formed through chemical reaction. The new $MgAl_2O_4$ buffer layer has the same crystal structure with the original MgO substrate other than the lattice parameter being twice that of the original one. Comparing the experimentally determined orientation relationships with the theoretically predicted orientation relationships, it is clear that the predictions from the edge-to-edge matching model are consistent with the experimental results. Theoretically, a good matching interface is more effective in triggering the nucleation of a new crystal. The detected nucleation undercooling of Al/MgO in this study is also confirmed by the results from Al/ $MgAl_2O_4$.

5. Conclusion

In this study, thermal analysis and high resolution transmission electron microscopy were used to study the nucleation behavior of high purity liquid Al on single crystal MgO substrates by measuring the undercooling and the crystal orientation relationship between nuclei and substrate. The results show that, due to the chemical reaction between liquid Al and substrates, the original substrate MgO would be completely replaced by reaction product $MgAl_2O_4$. Consequently, the detected undercooling is controlled by the newly produced $MgAl_2O_4$. The interface characterization of different exposed planes was observed by HRTEM, which is supported by a well-defined orientation relationship with the equivalent lattice misfit of 1.17%, and the orientation relationships of $(100)_{MgO}$ // $(100)_{MgAl2O4}$ // $(100)_{Al}$; $(110)_{MgO}$ // $(110)_{MgAl2O4}$ // $(110)_{Al}$ and $(111)_{MgO}$ // $(111)_{MgAl2O4}$ // $(111)_{Al}$.

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(1) Only $MgAl_2O_4$ layer is produced at the interface of Al/MgO system due to chemical reaction occurred from 750^{o}C to 660 ^{o}C.

(2) The well-defined orientation relationship is achieved at the interface of Al/ $MgAl_2O_4$/MgO.

(3) $MgAl_2O_4$ layer has a significant influence on the heterogeneous nucleation of Al.