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Solid-state Reaction of CaO Particles Dispersed in Powder Metallurgy Magnesium Composites †

FUJITA Junji*, ENAMI Keitaro, OHARA Masaki**, IGARASHI Takanori** and KONDOH Katsuyoshi*****

Abstract

Powder metallurgy magnesium composites reinforced with calcium oxides (CaO) were fabricated by using an equal channel angular bulk mechanical alloying process (ECABMA), using AZ series alloys (AZ31B, AZ61B, AZ91D) as the matrix material. In-situ formed compounds were investigated by XRD, DTA and SEM/EDS analysis. In the case of AZ61B added with CaO particles, the fabrication of Al_2Ca *and MgO occurred by reducing CaO during annealing the composite. Annealing treatment for longer time or at higher temperature is necessary for the reaction in the specimens with lower CaO content. For example, with 2.5 vol.% CaO added AZ61B, the* Al_2Ca *phase was synthesized by annealing at 550℃ for 1 hour or at 450℃ for 24 hours. Both kinds of Al atoms which exist in solid solution in α-Mg matrix at room temperature and which generated from the decomposition of* $Mg_{17}Al_{12}$ *phase (β phase) form* Al_2Ca *phase during annealing at elevated temperature.*

KEY WORDS: (Magnesium alloy), (Calcium oxide), (Bulk mechanical alloying), (AZ61B)

1. Introduction

Magnesium alloys are attractive materials as structural components in Personal Digital Assistant (PDA), motorcycles, automotives and aircrafts. This is because they are the lightest industrial metals in the practical use, and have high specific tensile strength. When using Mg alloys for engine components of automotives, superior heat resistances such as high temperature strength and creep properties are strongly required. It is, however, well known that the tensile strength of Mg alloys drastically decreases at elevated temperatures(1), and this prevents their widespread use in the automotive industry. Therefore, it is necessary to improve the heat resistance of Mg alloys.

The dispersion of second phases, such as oxides or intermetallic compounds which are thermally stable at elevated temperature, is effective for improving the mechanical properties at elevated temperatures because they prevent grain coarsening by their pinning effect or forming network structure at the grain boundaries. Previous studies have shown that creep properties of AZ91 alloys produced by the thixomolding process were improved by calcium (Ca) addition because of the formation of network-structured Al_2Ca intermetallic phases at the grain boundaries(2). In this study, calcium oxide (CaO) particles were employed instead of Ca additives, and dispersed in AZ series alloys (AZ31B, AZ61B and AZ91D) via a powder metallurgy (P/M) process. CaO is thermodynamically stable compared to other metallic oxides, and results in no reaction with Mg at elevated temperature. Furthermore, CaO is a readily available and cheap material. So, high performance Mg alloys reinforced with CaO particles can be cost-effective composites, and more widely applied to structural components in the automotive industry. To fabricate CaO/Mg-Al composites by the P/M process, bulk mechanical alloying processes(3) were employed in the present study. The microstructure changes of the Mg composites by heat treatment at elevated temperature were investigated, and the thermodynamical consideration for solid-state reaction was carried out.

2. Experimental

2.1 ECABMA process

AZ31B, AZ61B and AZ91D chips of about 2.5 mm or less length, machined from cast ingot materials, were employed as raw materials. CaO particles were prepared by milling the CaO blocks with purity of 98% or more, and used as additives. The elemental mixtures of Mg alloy chips and CaO particles were mechanically fractured and mixed in the die installed in the hydraulic press by using an equal channel angular bulk mechanical

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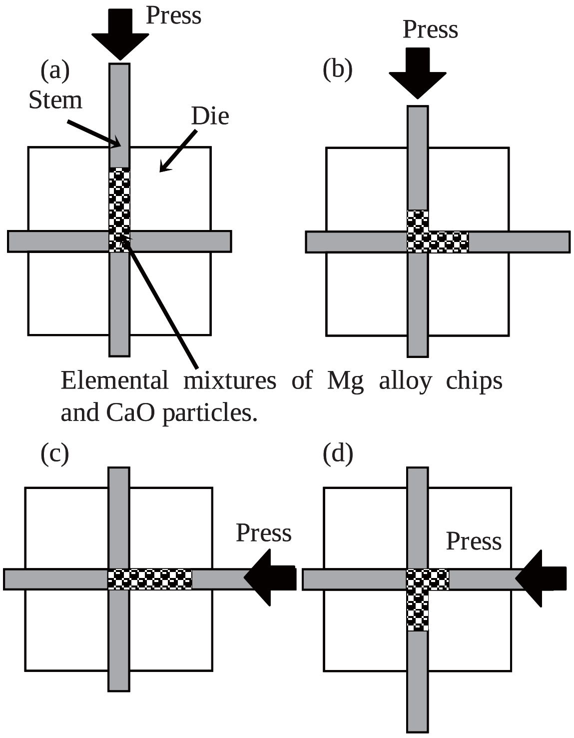


Fig.1 Schematic illustrations of ECABMA process used in this study.

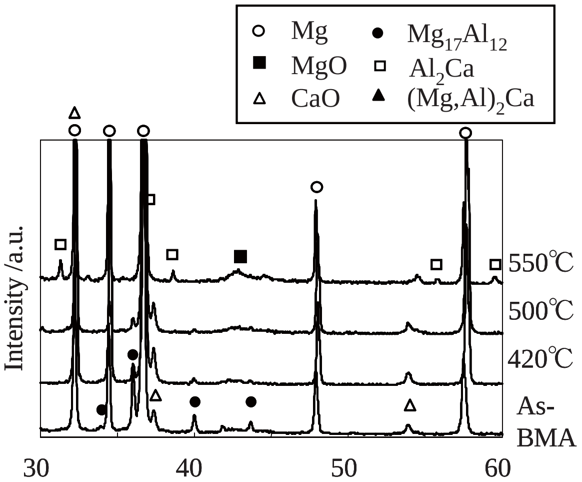
alloying (ECABMA) process, where the content of CaO additives was 2.5, 5, 7.5 and 10 vol.%. Figure 1 shows schematic illustrations of ECABMA process. The mixed powders were filled into the cross-shape die, and compacted and extruded within a channel bent through an angle 90 degree at room temperature as shown in (a) and (b). This process was counted as one pass of BMA. Figure 1(c) and (d) show the process from the right direction. The same deformation process was repeated from four directions, and this was counted as one cycle. The repetition of this process induced large strain in the mixed powders, and homogeneously dispersed CaO particles in the chips. After 50 cycles in BMA, a green compact billet with a cylinder shape, having 35 mm diameter and 80 mm length, was fabricated in the die.

2.2 Heat treatment and evaluation

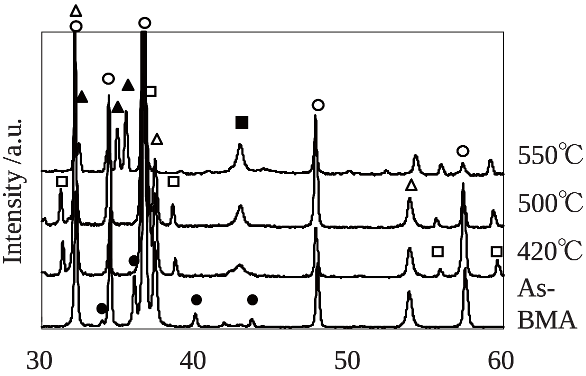
In order to investigate the microstructure changes, an annealing treatment was applied to the green compact specimen (as-BMA). The annealing temperatures range was from 300℃ to 625 ℃ in Ar gas atmosphere. The heating time at each temperature was 1 to 24 hours. X-ray Diffraction (XRD, Shimadzu, XRD-6100) analysis and FE-SEM (Field-Emission Scanning Electron Microscope, JEOL, JSM-6500F) with EDS (Energy Dispersive Spectrometry, JEOL, EX-64175JMU) analysis were carried out to investigate phase changes and microstructures on each ECABMA specimen. The thermal behavior due to microstructure changes was investigated by DTA (Differential Thermal Analysis, SHIMADZU, DTG-60) analysis. The heating rate was 10 ℃/min until 700℃ and the atmosphere was Ar gas.

3. Results and Discussion

Figure 2 shows XRD patterns of as-BMA billet of AZ61B containing 2.5 and 10 vol.% CaO particles before and after annealing. Annealing time was 4 hours for 420℃ and 500℃, and 1 hour for 550℃. In both materials, no oxidation of the specimen occurred during annealing because of no peak of magnesium oxide (MgO) at $2\theta=43^\circ$ after annealing at 420℃ and 500℃ as shown in Fig.2(a). AZ61B alloys with 2.5 vol.% CaO, annealed at 550℃, shows the decomposition of CaO and the formation of Al_2Ca intermetallic compound and MgO. On the other hand, AZ61B billets with 10 vol.% CaO annealed at 420℃ and 500℃ reveal Al_2Ca diffraction peaks, which disappear at 550℃ annealing temperature. At this temperature, $(Mg,Al)_2Ca$ compounds are formed, and CaO diffraction peak at $2\theta=37^\circ$ is not confirmed. Figure 3 shows SEM observation on as-BMA AZ61B specimen containing 10 vol.% CaO before and after annealing. CaO particles are homogeneously dispersed in as-BMA specimen as a result of the 50 cycles of the ECABMA process. After annealing at 500℃, it consists of four kinds of phases: α-Mg, CaO, MgO and Al_2Ca, as shown in Fig.2(b). Fig.3(b) indicates that Al_2Ca compounds have a spherical shape, and are dispersed in α-Mg matrix. In the case of the specimen annealed at 550℃, α-Mg, MgO and $(Mg,Al)_2Ca$ phases are detected, and $(Mg,Al)_2Ca$ phase is not spherical in shape. Figure 4 shows DTA profile of AZ61B containing 10 vol.% CaO particles produced via ECABMA process. The first peak, observed at about 525℃, corresponds to an endothermic reaction due to the decomposition of Al_2Ca phase. The second peak, observed at about 580℃ is due to the melting α-Mg phase. It means that Al and Ca generated by Al_2Ca changes into $(Mg,Al)_2Ca$ during solidification after annealing at 550℃. Thus, AZ61B containing each content of CaO particles shows the formation of Al_2Ca with the reductive decomposition of CaO. According to the Ellingham Diagram[4], CaO is the most thermally stable of the metal oxides, so it is not possible to reduce CaO in Mg-Al alloys. Thermodynamical consideration for the deoxidization mechanism of CaO was carried out by referring to thermodynamic data sheet[5]. Table 1 shows changes of the standard Gibbs free energy (ΔG) at 427℃ of the possible chemical reactions in this study. Equation (1) and (2) are rearranged as equation (3). The ΔG value of equation (3) is positive. So, deoxidization of CaO by Mg can not occur at 427℃ from a thermodynamical point of view. In the case of the Mg-Al-CaO system, however, reaction (4) can occur at this temperature because the ΔG value is negative (-172.3 kJ/mol). Figure 5 shows the relationship between temperatures and ΔG values of possible reductive reactions of CaO calculated from thermodynamic data sheets. It indicates that reaction (4) can occur at temperatures ranging from room temperature to 1500℃ because the ΔG value of this reaction is constantly negative. Accordingly, CaO can be decomposed under the condition that Al_2Ca compound is formed.



(a) AZ61B alloy with 2.5vol.% CaO.



(b) AZ61B alloy with 10vol.% CaO.

Fig.2 XRD profiles of P/M AZ61B alloys containing CaO particles via ECABMA after annealing at 420℃ and 500℃ for 4 hours, and at 550℃ for 1 hour.

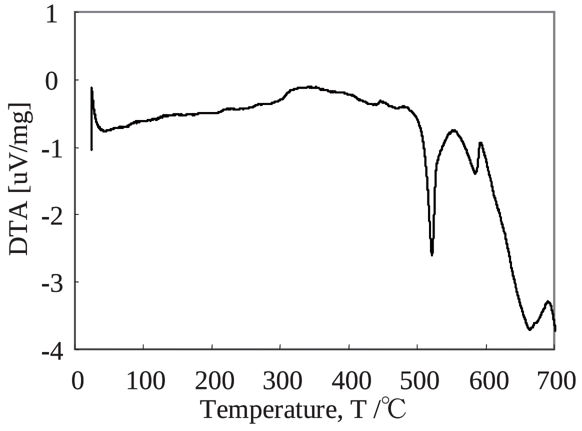


Fig.4 DTA profile on P/M AZ61B alloy containing 10 vol.% CaO particles via ECABMA.

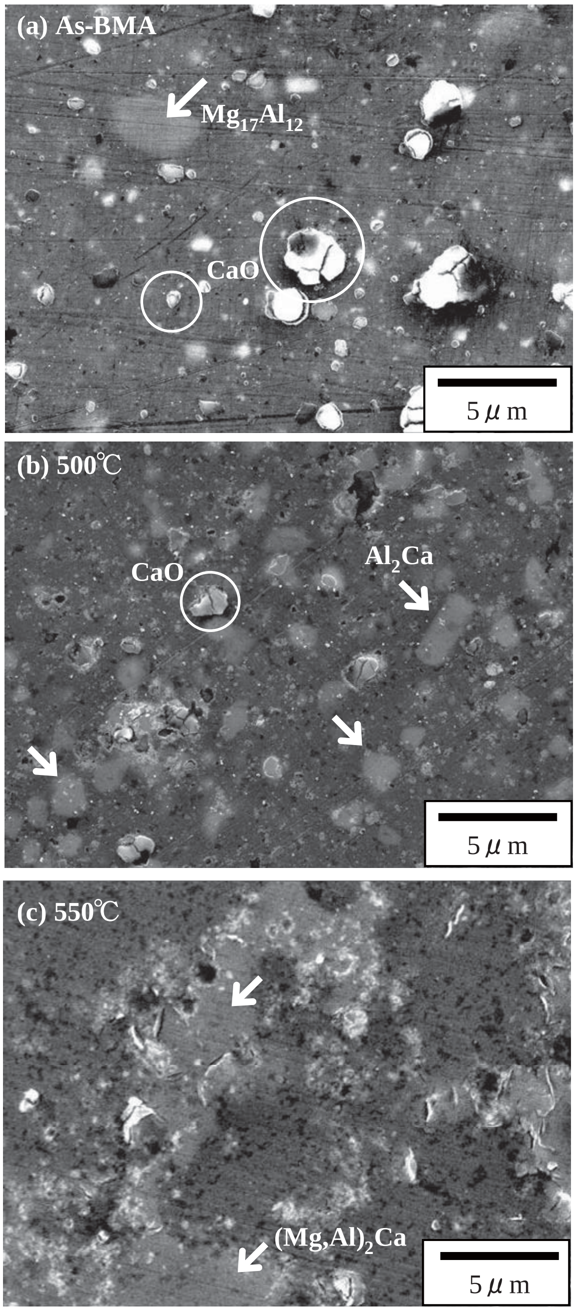


Fig.3 SEM observation on P/M AZ61B alloy containing 10 vol.% CaO particles via ECABMA: as-BMA(a), after annealing at 500℃(b) and 550℃(c).

Table 1 Changes of Gibbs free energy at 427℃ of possible chemical reaction in this study[5)].

Chemical reaction	$\Delta G_{427℃}$ [kJ/mol]
(1) $2Mg + O_2 = 2MgO$	-1046.7
(2) $2Ca + O_2 = 2CaO$	-1123.4
(3) $Mg + CaO = Ca + MgO$	38.4
(4) $Mg + 2Al + CaO = Al_2Ca + MgO$	-172.3

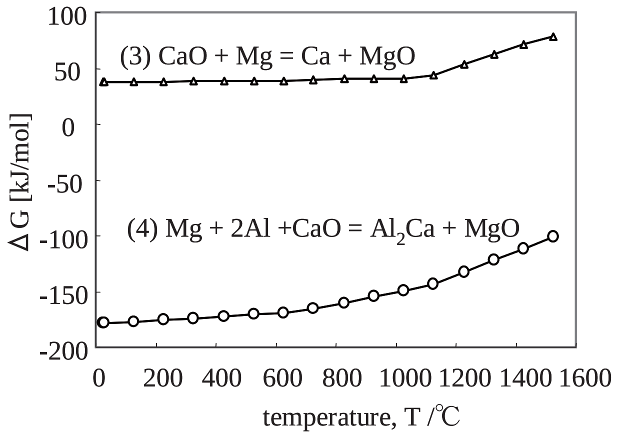


Fig.5 Changes of the standard Gibbs free energy (Δ G) of the possible chemical reaction in Mg-Al-CaO system[5)].

Figure 6 shows XRD patterns of AZ61B BMA specimen containing 2.5vol.% CaO after annealing at 400℃, 450℃ and 500℃ for 24 hours. Although this specimen does not indicate reaction (4) after annealing at 500℃ or less for 4 hours as shown in Fig.2(a), 24 hours annealing treatment at 450℃ and 500℃ drives the reaction. Thus, the progress of reaction (4) is largely influenced by temperature and time, and annealing treatment for longer time is necessary for the formation of Al_2Ca with the reductive decomposition of CaO at lower temperature. It means that reaction (4) in CaO/Mg-Al composite by P/M process is governed by diffusion behavior of Al atomic element. On the other hand, under the conditions of a given temperature, annealing treatment for longer time causes the progress of reaction (4) in specimens containing less CaO particles. This is because, in specimens with lower CaO content, the average distance between one Al atom and one CaO particle is longer and the probability of one Al atom reaching CaO particles within a given length of time is lower. So, longer time is necessary for Al to contact CaO sufficiently.

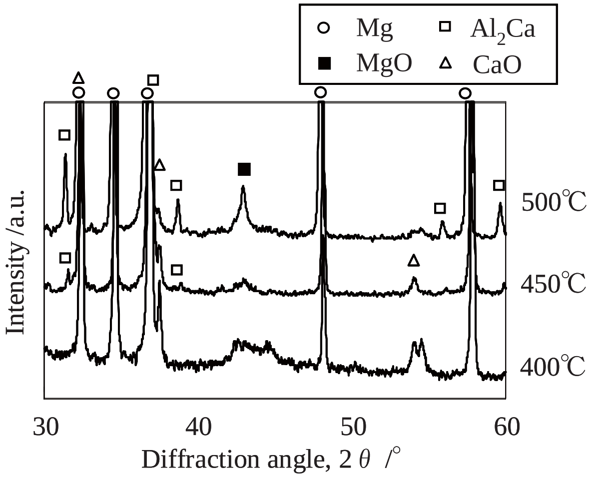
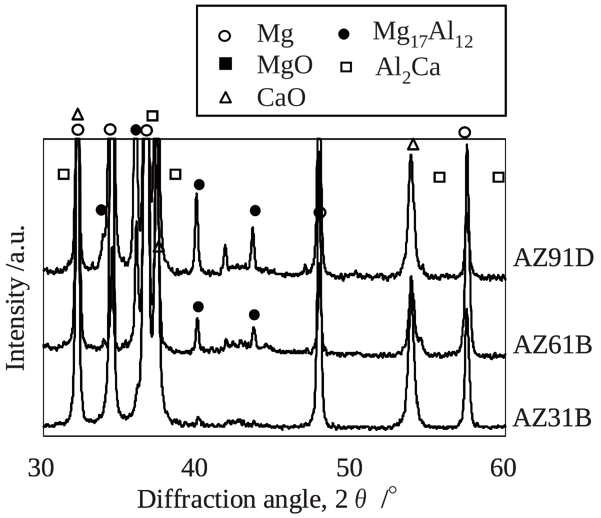
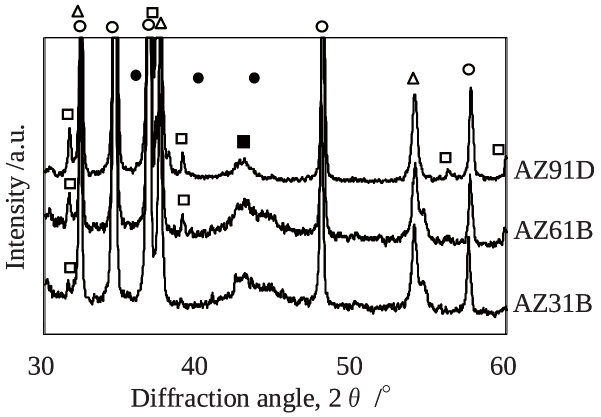


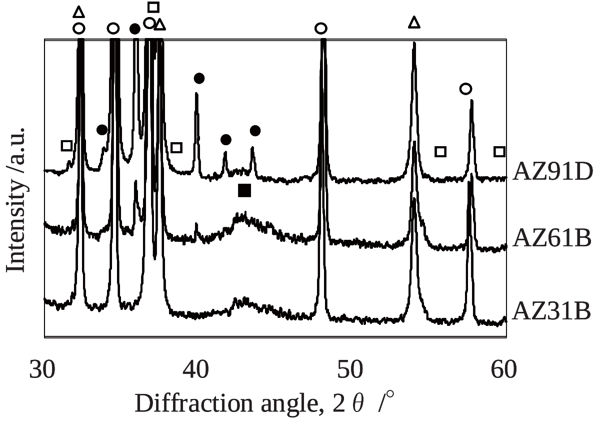
Fig. 6 XRD profiles of P/M AZ61B alloys containing 2.5vol.%CaO particles via ECABMA after annealing at elevated temperature for 24 hours.



(a) As-BMA specimen.



(b) Annealed at 360℃.



(c) Annealed at 300℃.

Fig.7 XRD profiles of P/M AZ series alloys containing 10 vol.% CaO particles via ECABMA: as-BMA (a), after annealing for 24 hours at 360℃ (b) and 300℃ (c).

Figure 7 shows XRD patterns of as-BMA billet of AZ31B, AZ61B and AZ91D containing 10 vol.% CaO particles before and after annealing for 24 hours. No Al_2Ca compound is formed in each as-BMA specimen. Each specimen indicates Al_2Ca diffraction peak at 2θ

Table 2 Al composition of matrix phase of as-BMA billets of AZ series alloys with CaO particles and pure Mg powder measured by SEM-EDS point analysis.

Base alloy	Mg powder	AZ31B	AZ61B	AZ91D
Al composition /at.%	1.50	3.43	5.86	7.22

=31.5° at 360℃ annealing temperature, and only AZ91D/CaO composite also indicates the same peak at 300℃. DTA analysis and high temperature XRD analysis reveal that melting point of $Mg_{17}Al_{12}$ phase (β phase) in AZ61B and AZ91D alloy is about 320℃ and 440℃, respectively. So, during annealing AZ61B/CaO composite at 360℃, all of Al atoms which AZ61B alloy contains were diffused in α-Mg matrix by the decomposition of β phase, and reacted with CaO particles. In the case of AZ61B/CaO composite annealed at 300℃ and AZ91D/CaO composite annealed at 300℃ and 360℃, β phase did not completely decompose. The formation of Al_2Ca, however, also occurred in AZ91D/CaO composite after annealing at 300℃ or 360℃, as shown in Fig.7. Table 2 shows Al composition of matrix phase of as-BMA billets measured by SEM-EDS point analysis. 20 numbers of measurement were carried out except for β phase and large CaO particles, and the mean values were used. Al composition of pure Mg powder indicates 1.50 at.%, which is the measuring limit of SEM-EDS. Table 2 reveals that Al atoms in solid solution exists in matrix phase of as-BMA billets of AZ31B, AZ61B and AZ91D with 10 vol.% CaO. So, in AZ91D/CaO composite, the formation of Al_2Ca can occur at 300℃ and 360℃ annealing temperatures, where β phase does not decompose. Fig.7 reveals that AZ61B and AZ31B with 10 vol.% CaO indicate no Al_2Ca diffraction peak after annealing at 300℃. As shown in Table 2, Al composition of AZ31B, AZ61B and AZ91D containing 10 vol.% CaO increases in that order. So, no enough amount of Al atoms contacted CaO particles by diffusion in AZ31B/CaO and AZ61B/CaO composite, and Al_2Ca diffraction peaks were not detected.

4. Conclusions

Phase changes of P/M AZ series alloys with added CaO particles via the ECABMA process were investigated, and the thermodynamical consideration for this system was examined. It can be concluded that:

(1) In the case of AZ61B/CaO composites, the formation of Al_2Ca and MgO occurred by reducing CaO during annealing the composite. This reaction was governed by Al diffusion to CaO particles in α-Mg matrix. So, it could more easily occur at the higer annealing temperature for the longer annealing time and in the specimen with higher content of Al atoms or CaO particles. On the other hand, with 10 vol.% CaO added to AZ61B, Al_2Ca compound was decomposed, and $(Mg,Al)_2Ca$ phase was formed by annealing at about 550℃ or more.

(2) Both kinds of Al atoms which exist in solid solution in α-Mg matrix at room temperature and which generated from the decomposition of β phase form Al_2Ca phase during annealing at elevated temperature.

(3) From a thermodynamical point of view, the deoxidization of CaO can occur under the condition that Al_2Ca compound is formed, in spite of its stability.

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