

REACTION OF SOME OXIDE CERAMICS WITH MOLTEN ALUMINUM

Yutaka Ohya, Yusuke Ishii and Takayuki Ban
Gifu University, Gifu 501-1193, Japan

ABSTRACT

TiO₂, Y₂Ti₂O₇, Y₂O₃ and MgO ceramics are immersed into molten aluminum at 1000°C for 25h and reaction of the ceramics was investigated. According to an “Ellingham diagram” TiO₂ should be reduced and, MgO and Y₂O₃ should not be reduced by molten aluminum. In an actual reaction of these ceramics with molten aluminum, a reaction at the interface between them is very important. At the interface of TiO₂ and Y₂Ti₂O₇, corundum layer was formed and this layer prevents further reaction. Y₂O₃ and MgO ceramics were reacted with Al to make aluminum oxide compounds.

1. INTRODUCTION

Molten aluminum is very reactive and it reduces many oxide ceramics and we have reported to use Al₂TiO₅ ceramics as a refractory material^[1,2]. In order to prevent and/or expect the reduction reaction of oxides by molten aluminum, an “Ellingham diagram” offers crucial guide and is usually used for a selection and modification of the refractory materials. According to the Ellingham diagram, TiO₂ should be reduced and, MgO and Y₂O₃ should not be reduced by molten aluminum. But an actual reaction of the oxide ceramics with molten aluminum is not straightforward. Sometimes reaction interface between them is very important to prevent the reduction reaction. Furthermore, a compound of Y₂Ti₂O₇ consists of TiO₂ and Y₂O₃, and the reaction of this with molten aluminum is very interesting. Here we report our results of studies of reactions of TiO₂, Y₂Ti₂O₇, Y₂O₃, and MgO ceramics with molten aluminum.

2. MATERIALS AND METHODS

Raw materials used were TiO₂, Y₂O₃ and MgO powders of high purity, >99.9%, and they were CIPed into disks of 10 mm diameter by 100 MPa and then fired at 1500°C for 2h to obtain dense ceramics. The relative densities of the TiO₂, Y₂O₃ and MgO ceramics were 85, 94 and 93%, respectively. The Y₂Ti₂O₇ ceramic was fabricated by mixing TiO₂ and Y₂O₃ in a ball mill, and CIPed, then fired at 1500°C 2h. The resultant Y₂Ti₂O₇ ceramic was 83% of its theoretical density. The fired ceramic was set in an alumina tube. Aluminum rod, 99% pure and 5.5g, was set on the ceramic in the alumina tube. Then it was heated at 1000°C for 25h in N₂ gas flowing atmosphere. After the reaction experiment, it was cut and polished for microstructural observation using SEM and EDX. Another sample after the reaction was treated with aqueous NaOH solution to remove aluminum and the samples as well as the sediments were analyzed.

3. RESULTS AND DISCUSSION

3-1. Reaction of TiO₂ and Ti₂Y₂O₇ ceramics with molten Al

Among the four oxide ceramics tested, TiO₂ and Y₂Ti₂O₇ were not reacted severely. Figure 1 shows SEM and EDX results of TiO₂ ceramics after the test. The interface between the aluminum and TiO₂ ceramics is very clear and the both

constituents, Al and Ti, were not reacted with each other. An EDX signal of oxygen was observed at the interface and in TiO₂ region. It is obvious that the oxidized aluminum layer existed at the interface and prevented the reaction. In order to identify the crystalline phase of the layer, XRD measurement of aq. NaOH treated sample was conducted and the result is shown in Fig. 2. It reveals that corundum phase was crystallized on the surface, though corundum hardly crystallize at 1000°C under usual condition. Beside corundum, strong peaks of rutile and many unidentified peaks are existed. The unidentified peaks should be from oxide-deficient titania phases, TiO_{2-x}. The black color of sample after the test shown by an inserted photo in Fig. 2 confirms the partial reduction of TiO₂. The existence of corundum on the TiO₂ pellet means the contact between them is strong. The strong contact prevent the further reduction of Ti⁴⁺ by molten aluminum. The Al₂TiO₅ is not formed because this phase is thermodynamically stable only above 1280°C^[3].

In case of Y₂Ti₂O₇, the same result was obtained and corundum phase retarded the further reduction. The difference between TiO₂ and Y₂Ti₂O₇ was the thickness of corundum layer. The thickness of the former was less than 1μm and the latter was about 3 μm. These difference in the thickness often be caused by the porosity of the sintered sample, but relative density of the samples was about 83-85% of theoretical. The reactive nature of yttrium oxide, described in the next section, would bring the difference.

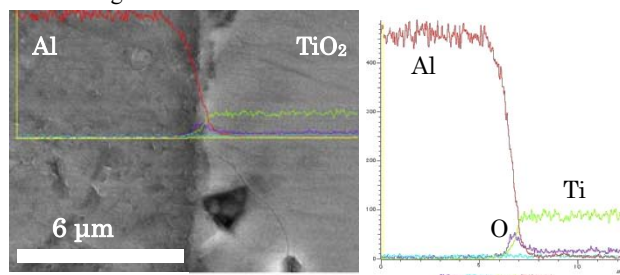


Fig. 1 SEM and EDX measurement of TiO₂-molten Al interface after reaction at 1000°C for 25h.

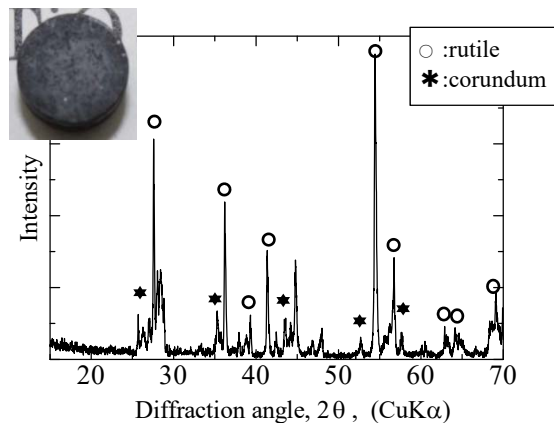


Fig. 2 XRD profile of TiO₂-molten Al interface after reaction at 1000°C for 25h. The aluminum was reached by aq. NaOH. The insert is a photo of the TiO₂ pellet after the test.

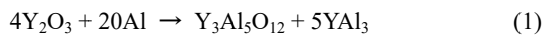
We have already reported that stable oxide, such as Mg-Al spinel protected Al_2TiO_5 ceramics against the reduction by molten aluminum^[1]. In that case the spinel layer was formed by reaction of magnesium in the aluminum alloy used for the test and oxide from Al_2TiO_5 ceramic. Present case corundum also play the same role of the protection.

3-2. Reaction of Y_2O_3 ceramic with molten Al

Thermodynamically, Y_2O_3 is very stable against reduction. Therefore it is applied and/or studied widely as a material of crucible for metal industries. But Y_2O_3 is also known to make intermetallic compound with aluminum and Y_2O_3 is easily reacted with molten aluminum to make both intermetallic compounds and yttrium aluminum oxides^[4,5,6]. Here we conducted the experiment of reaction of Y_2O_3 with molten aluminum.

The cut and polished surface after the reduction test was observed and shown in Fig. 3. Before the test Y_2O_3 pellet was dense of 94% but after the test it became porous and bright matter was observed in aluminum. The structure is the same as the previous reports. The bright matter should be intermetallic compound of Y and Al. This intermetallic compound was crystallized during cooling and at the reaction temperature, 1000°C, it is liquid of aluminum and yttrium, according to the phase diagram of Al-Y and molar ration of used Al and Y. After treatment with aq. NaOH, the crystalline phases of the remain of the pellet and sediment were examined. The sediment is confirmed to be YAl_3 with space group of $R\bar{3}m$ and the remain of the pellet consists of $\text{Y}_3\text{Al}_5\text{O}_{12}$, garnet structure, and orthorhombic YAlO_3 phase, they are shown in Fig. 4 and 5, respectively.

The size of the remain of the pellet after aq. NaOH treatment is almost the same as that of the sample before reaction test, as listed in Table 1. The mass decreased by about 30%. This decrease was caused by the reactions below,



In the reactions Y_2O_3 is reduced by molten Al to form $\text{Y}_3\text{Al}_5\text{O}_{12}$ and/or YAlO_3 , and Y component diffused outside the pellet. The mass change of Y_2O_3 to $\text{Y}_3\text{Al}_5\text{O}_{12}$ or YAlO_3 accompanies decrease of 27%. This is almost the same as the obtained value. The reaction also causes the volume reduction by 27 and 32% for formation of $\text{Y}_3\text{Al}_5\text{O}_{12}$ and YAlO_3 , respectively, based on the density of Y_2O_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$, and YAlO_3 being 5.03, 5.35 and 4.55 g/cm^3 , respectively and molecular weight. This large decrease in the volume is a key to form the porous pellet after the reaction and continuous reaction throughout the pellet. A semi-quantitative image analysis of the SEM photo results in the pore volume of about 40% and the pores make continuous channel from inside to the surface. By the reaction of Y_2O_3 with Al, formed metallic Y constituent diffused though the channel to outside into the molten Al. This is not expected from the Ellingham diagram, because the diagram does not include any information on intermetallics, such as YAl_3 , and liquids.

Table 1 Change in size and mass of sample after reduction test and treating with aq. NaOH.

	Diameter / mm	Thickness / mm	Mass / g	Density / g cm^{-3}
As-sintered	7.51	4.65	0.964	4.69
After test	7.51	4.59	0.688	3.39

3-2. Reaction of MgO ceramic with molten Al

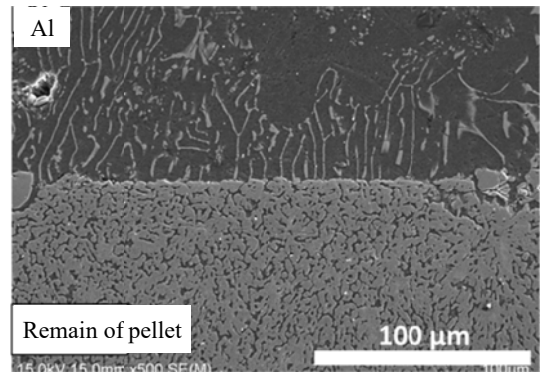


Fig. 3 SEM micrograph of polished surface of Y_2O_3 -molten Al interface after reaction at 1000°C for 25h.

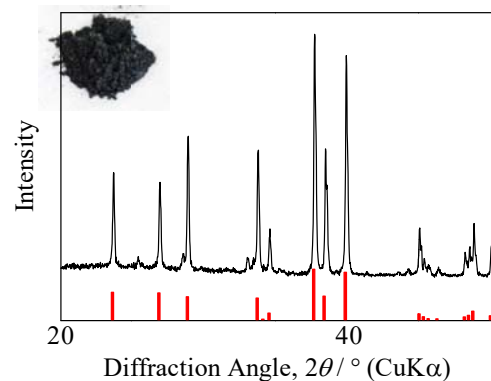


Fig. 4 XRD profile of sediment by treatment with aq. NaOH after reaction of Y_2O_3 -molten Al. The insert is a photo of the sediment. Bars: YAl_3 ; $R\bar{3}m$ from JCPDS card.

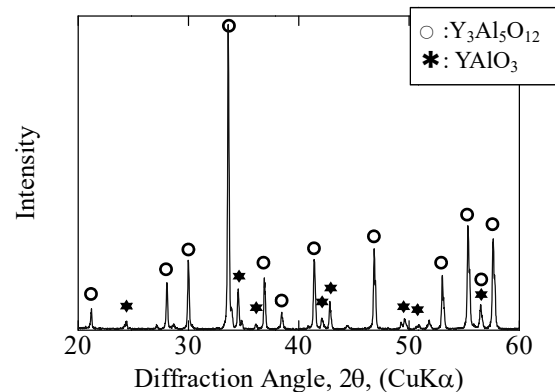
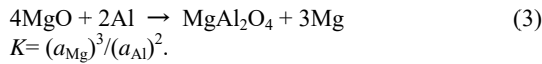


Fig. 5 XRD profile of Y_2O_3 pellet surface after treatment with aq. NaOH after reaction of Y_2O_3 -molten Al.

MgO ceramic also expects to have strong resistance against reduction in molten aluminum. After the reduction test the sample within the alumina tube was cut and polished. Figure 6 is photographs and a schematic drawing of it. An outer diameter of the alumina tube used is 14mm. The outer side of the MgO ceramic became dark gray to black and the thickness was about 0.9 mm. Observation by optical microscope, cracks exist at the boundary of black part and white central part. After the treatment with aq. NaOH, the MgO ceramics was easily broken into central white block and outer black grains, as shown in Fig. 7. XRD measurement, which is not shown here, of these parts reveals that the outer part is Al_2MgO_4 spinel and white central part is unreacted MgO. The cracks exists at the boundary between spinel and MgO, which is often observed in the experiment of reaction couple of Al_2O_3 and MgO to form spinel by diffusion and solid state reaction of them^[7].

The reaction and equilibrium constant K are simply considered as next equations.



Where a_{Mg} and a_{Al} are activities of Al and Mg in the liquid. That of MgO and MgAl_2O_4 is considered to be unity, though spinel may form solid solution. Since $\Delta_r G^\circ$ of the reaction is calculated to be 66 kJ at 1298K, next equations are derived at the equilibrium.

$$\Delta_r G = \Delta_r G^\circ + RT \ln K = 0,$$

then

$$66 \text{ kJ} = -RT \ln (a_{\text{Mg}})^3 / (a_{\text{Al}})^2$$

and

$$(a_{\text{Mg}})^3 / (a_{\text{Al}})^2 = 0.0022.$$

If activity of the components is assumed to be equal to their molar fractions in the liquid, $(a_{\text{Mg}})^3 / (a_{\text{Al}})^2 = 0.00223$ when $a_{\text{Mg}} = 0.12$. The value seems not so difficult to be achieved. Results of SEM and EDX analysis at the interface between Al and spinel layer is shown in Fig. 8. Semi-quantitative EDX analysis of the marked point in Fig. 8 shows the composition of 91.2% Al, 3.5% Mg and 5.3% O. In the aluminum, several percentage of Mg is dissolved. By the EDX, an obvious evidence of existence of alumina phase is not detected. Metallic Al is directly contacted with spinel layer. XRD experiment of the MgO pellet after aq. NaOH treatment also suggests the direct contact, because only very small peaks of corundum are detected, which is not shown here.

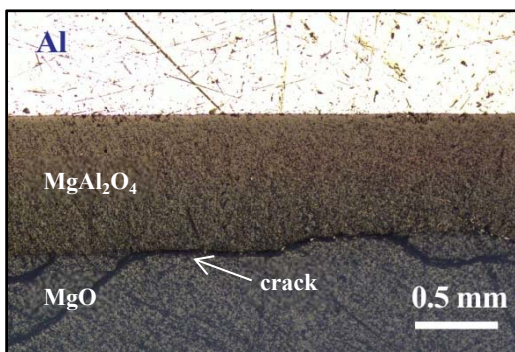
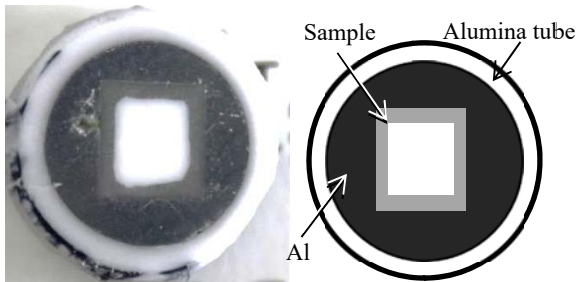


Fig. 6 Cut and polished section of MgO-Al reaction test. Upper left: photo, upper right: schematic drawing, lower: optical micrograph.



Fig. 7 Crushed MgO pellet after the reduction test.

The aluminum after the reduction test was treated with aq. NaOH and the residual was examined by XRD and shown in Fig. 9. Crystalline phase of aluminum magnesium hydroxide, $\text{Mg}_2\text{Al}(\text{OH})_7$, is detected besides $\text{Al}(\text{OH})_3$. This also confirmed the formation of dissolving Mg from MgO pellet into molten Al.

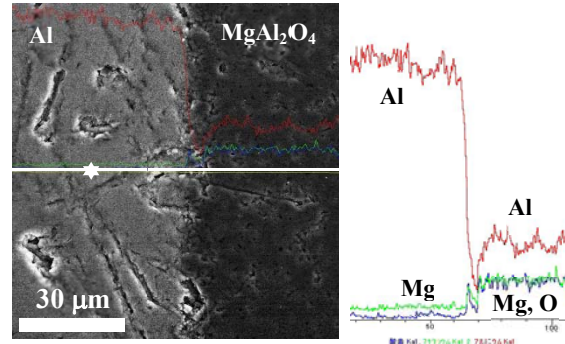


Fig. 8 SEM and EDX measurement of MgO-molten Al interface after reaction at 1000°C for 25h.

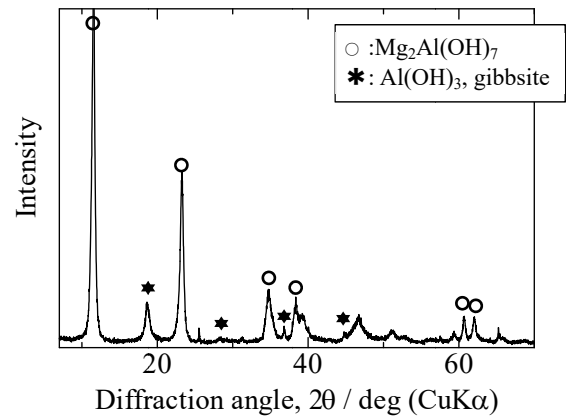
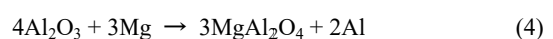


Fig. 9 XRD profile of sediment by treatment with aq. NaOH after reaction of MgO-molten Al. No marked peaks are not identified.

Spinel layer is also formed on the surface of the alumina tube, as shown in Fig. 10. But its thickness is about 80 μm , one tenth of the spinel layer on MgO pellet. Reaction of corundum with MgO to form spinel has been studied extensively as a typical solid state reaction^[7]. When single crystal and/or polycrystal of corundum and MgO are contacted at high temperature, spinel forms at the interface. The reaction rate is considered to be controlled by diffusion of 3Mg^{2+} and 2Al^{3+} to opposite direction. The thickness of formed spinel is about 500 μm around 1500°C and soaking for 100-200h. The thickness ratio of spinel on MgO side and corundum side is 1:3 to 1:4, corundum side is thick.

Comparing those data of the solid state reaction with the present case, thickness of the formed spinel is quite large, about 0.9 mm at 1000°C for 25h. And spinel formed at MgO side is thicker than that of corundum side. In general reactions with liquid phase may proceed faster than solid state reactions. The present reaction, however, is controlled by diffusion of cations, 3Mg^{2+} and 2Al^{3+} , through spinel phase and this diffusion seems independent on the circumstance, whether liquid phase exists or not.

On the surface of alumina tube the formation of spinel follows next equation.



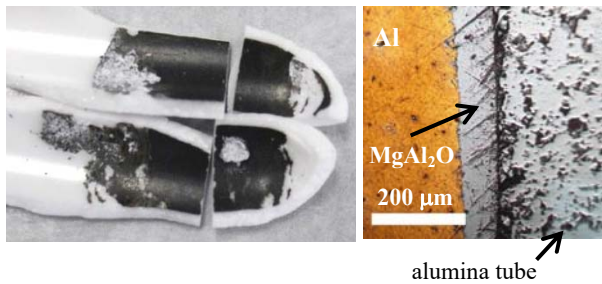


Fig. 10 Alumina tube after the reaction test. Black layer is spinel, measured by XRD, left photo. And spinel layer on alumina tube, right.

$\Delta_r G^\circ$ of the reaction (4) is -258 kJ at 1298 K and this reaction is favorable than the reaction of spinel formation on MgO side. If the both reactions of the spinel formation on corundum and MgO sides are considered as 'half reactions', spinel formation on corundum side determines the reaction rate of spinel. Because diffusion process of cations in spinel phase could be regarded as the same in both half reactions, the spinel formation reaction at corundum surface is the control process of the reaction. But this consideration contradicts many previous studies. The formed spinel is dark gray to black and it suggests that the spinel contained many defects to accelerate ion diffusion. If so, this is very interesting to make spinel at lower temperature and short time. In case of Al_2TiO_5 ceramics, thin spinel layer is formed on the surface of the ceramics and this layer prevent the further corrosion. But present MgO pellet is not the case. This is because there are too much MgO to form spinel in present case.

4. CONCLUSION

Reaction of TiO_2 , $\text{Y}_2\text{Ti}_2\text{O}_7$, Y_2O_3 and MgO with molten aluminum at 1000°C is investigated. Degree of reaction doesn't depend on the stability of the oxide against reduction. On the surface of TiO_2 and $\text{Y}_2\text{Ti}_2\text{O}_7$ ceramics, formed corundum layer prevents further reaction and Ti^{4+} is not reduced severely. Y_2O_3 pellet reacts with molten Al and, $\text{Y}_3\text{Al}_5\text{O}_{12}$ and YAlO_3 resulted. The reaction proceeds the entire of pellet. The volume decrease by the formation reaction of $\text{Y}_3\text{Al}_5\text{O}_{12}$ and/or YAlO_3 causes the result. Formation of liquid phase of Al and Y also enhances the reaction. Spinel formation reaction in the system of MgO-Al is very fast comparing the usual solid state reaction. The vary high rate of spinel formation and cracks at the interface between formed spinel and MgO make MgO ceramic to be not suitable for refractory of molten aluminum. Among the samples examined TiO_2 based ceramics have the best performance for the used of refractory for molten aluminum.

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