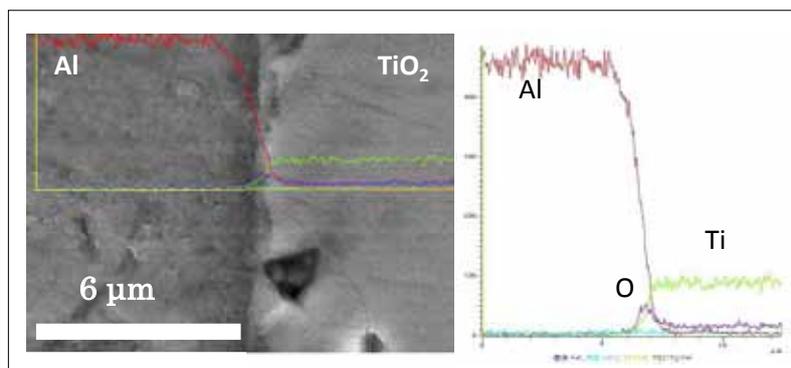# Reaction of some Oxide Ceramics with Molten Aluminium

Y. Ishii, T. Ban, Y. Ohya

TiO_2, $Y_2Ti_2O_7$, Y_2O_3 and MgO ceramics are immersed into molten aluminium at 1000 °C for 25 h and the reaction of the ceramics was investigated. According to an Ellingham diagram, TiO_2 should be reduced, and MgO and Y_2O_3 should not be reduced by molten aluminium. In an actual reaction of these ceramics with molten aluminium, a reaction at the interface between these ceramics and molten aluminium is very important. At the interface of TiO_2 and $Y_2Ti_2O_7$, a corundum layer was formed, and this layer prevents further reaction. Y_2O_3 and MgO ceramics reacted with Al to form oxide compounds, metallic Y, and Mg in molten aluminium.

1 Introduction

Molten aluminium is very reactive and it reduces many oxide ceramics and it was reported to use Al_2TiO_5 ceramics as a refractory material [1, 2]. In order to prevent and/or expect the reduction reaction of oxides by molten aluminium, an Ellingham diagram offers a crucial guide and is usually used for a selection and modification of the refractory materials. According to the Ellingham diagram, TiO_2 should be reduced and, MgO and Y_2O_3 should not be reduced by molten aluminium. But an actual reaction of the oxide ceramics with molten aluminium is not straightforward. Sometimes reaction interface between them is very important to prevent the reduction reaction. Furthermore, the diagram does not include intermetallic and multicomponent oxide compounds, and solid and/or liquid

Fig. 1 SEM and EDX measurement of TiO_2-molten Al interface after reaction at 1000 °C for 25 h

mixtures. Here are reported results of studies of reactions of TiO_2, $Y_2Ti_2O_7$, Y_2O_3, and MgO ceramics with molten aluminium.

2 Materials and methods

Raw materials used were TiO_2, Y_2O_3 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 2 h to obtain dense ceramics. The relative densities of the TiO_2, Y_2O_3 and MgO ceramics were 85, 94 and 93 %, respectively. The $Y_2Ti_2O_7$ ceramic was fabricated by mixing TiO_2 and Y_2O_3 in a ball mill and CIPed, then fired at 1500 °C for 2 h. The resultant $Y_2Ti_2O_7$ ceramic was 83 % of its theoretical density. The fired ceramic was set in an alumina tube. Aluminium rod, 99 % pure and 5,5 g, was set on the ceramic in the alumina tube. Then it was heated at 1000 °C for 25 h in N_2 gas flowing atmosphere. After the reaction, 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 aluminium and the samples as well as the sediments were analysed.

3 Results and discussions

3.1 Reaction of TiO_2 and $Ti_2Y_2O_7$ ceramics with molten Al

Among the four oxide ceramics tested, TiO_2 and $Y_2Ti_2O_7$ were not reacted severely. Fig. 1 shows SEM and EDX results of TiO_2 ceramics after the test. The interface between the aluminium and TiO_2 ceramics is very clear and both constituents, Al and Ti, did not react with each other. An EDX signal of oxygen was observed at the interface and in the TiO_2 region. It is obvious that the oxidized aluminium 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 crystallized on the surface, though corundum hardly crystallizes at 1000 °C under usual condition. Beside corundum, strong peaks of rutile and many unidentified peaks were present. The unidentified peaks should be from oxide-deficient titania phases,

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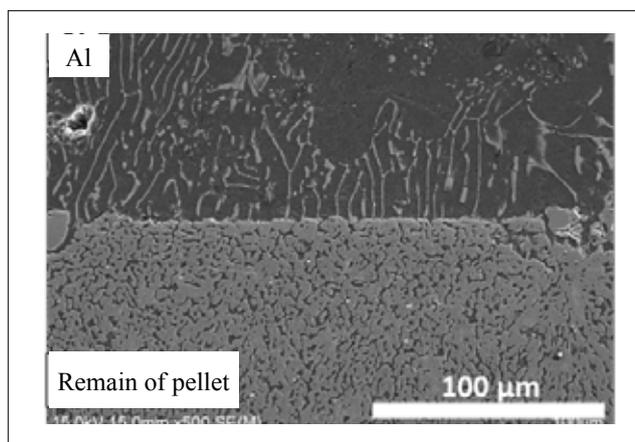*Gifu University*
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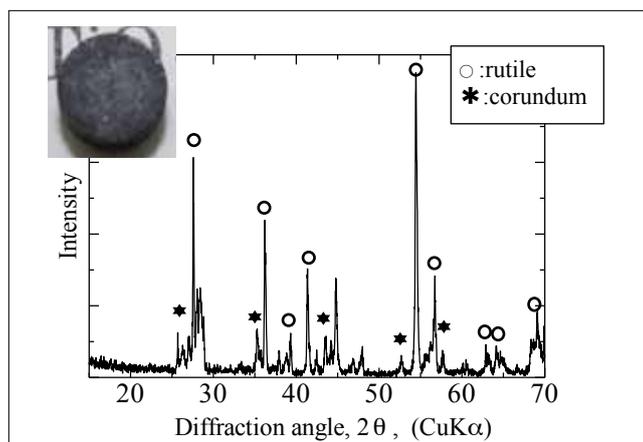
Fig. 2 XRD profile of TiO$_2$-molten Al interface after reaction at 1000 °C for 25 h. The aluminium was reached by aq. NaOH. The insert is a photo of the TiO$_2$ pellet after the test

Fig. 3 SEM micrograph of polished surface of Y$_2$O$_3$-molten Al interface after reaction at 1000 °C for 25 h

TiO$_{2-x}$. The black colour of the sample after the test shown by an inserted photo in Fig. 2 confirms the partial reduction of TiO$_2$. The existence of corundum on the TiO$_2$ pellet means the contact between them is strong. The strong contact prevents the further reduction of Ti^{4+} by molten aluminium. Al$_2$TiO$_5$ is not formed because this phase is thermodynamically stable only above 1280 °C [3].

In case of Y$_2$Ti$_2$O$_7$, the same result was obtained and corundum phase retarded the further reduction. The difference between TiO$_2$ and Y$_2$Ti$_2$O$_7$ was the thickness of corundum layer. The thickness of the former was less than 1 μm and the latter was about 3 μm. These difference in the thickness of reaction layer can often be caused by the porosity of the sintered sample, but there is no significant difference between their relative densities, about 83–85 % of the theoretical. The reactive nature of yttrium oxide, described in the next section, would bring the difference.

It was already reported that a stable oxide, such as Mg–Al spinel, protected Al$_2$TiO$_5$ ceramics against the reduction by molten aluminium [1]. In that case, the spinel layer was formed by reaction of magnesium in the aluminium alloy used for the test and oxide from the Al$_2$TiO$_5$ ceramic. In the present case, corundum also plays the same role of the protection.

3.2. Reaction of Y$_2$O$_3$ ceramic with molten Al

Thermodynamically, Y$_2$O$_3$ is very stable against reduction. Therefore, it is applied and/or studied widely as a crucibles material for metal industries. But Y$_2$O$_3$ is also known to develop intermetallic compounds with aluminium, and Y$_2$O$_3$ easily reactes with molten aluminium to develop both intermetallic compounds and yttrium aluminium oxides [4–6]. Here, the reaction experiment of Y$_2$O$_3$ with molten aluminium was conducted.

The cut and polished surface after the reduction test was investigated and shown in Fig. 3. Before the test, the Y$_2$O$_3$ pellet was dense of 94 %, but after the test it became porous and bright matter was observed in aluminium. 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 a liquid of aluminium 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 pellet and sediment were examined. The sediment is
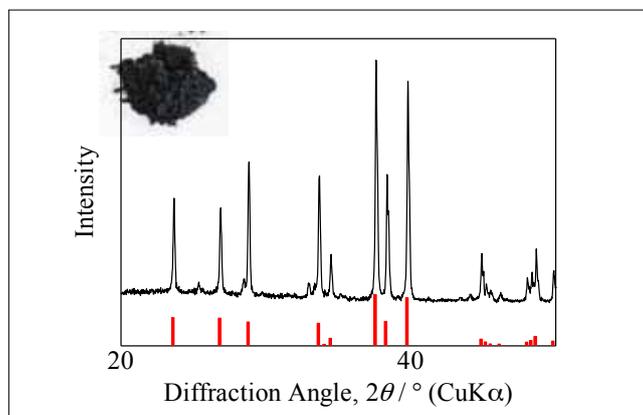
Fig. 4 XRD profile of sediment by treatment with aq. NaOH after reaction of Y$_2$O$_3$-molten Al. The insert is a photo of the sediment; bars: YAl$_3$: *R*-3m from JCPDS card
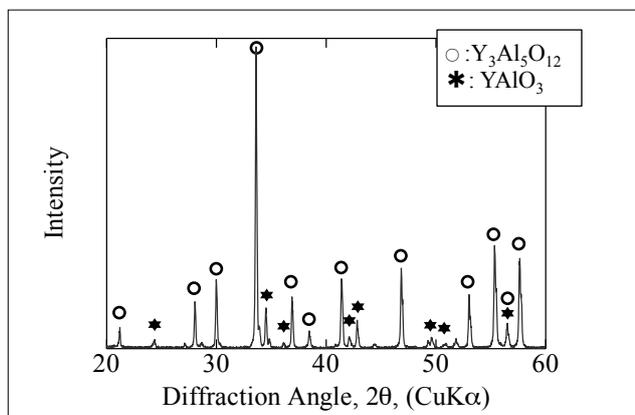

Fig. 5 XRD profile of Y$_2$O$_3$ pellet surface after treatment with aq. NaOH after reaction of Y$_2$O$_3$-molten Al

Tab. 1 Change in size and mass of the Y_2O_3 sample after reduction test and treating with aq. NaOH

	Diameter [mm]	Thickness [mm]	Mass [g]	Density [g/cm³]
As-sintered	7,51	4,65	0,964	4,69
After test	7,51	4,59	0,688	3,39

confirmed to be YAl_3 with space group of R-3m and the pellet remain consists of $Y_5Al_5O_{12}$, garnet structure, and orthorhombic $YAlO_3$ phase. They are shown in Fig. 4 and 5, respectively.

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

$$4Y_2O_3 + 20Al \rightarrow Y_3Al_5O_{12} + 5YAl_3 \quad (1)$$

$$Y_2O_3 + 4Al \rightarrow YAlO_3 + YAl_3 \quad (2)$$
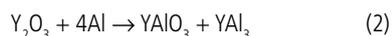
In these reactions, Y_2O_3 is reduced by molten Al to form $Y_3Al_5O_{12}$ and/or $YAlO_3$, and Y component diffused outsize the pellet. The mass change of Y_2O_3 to $Y_3Al_5O_{12}$ or $YAlO_3$ accompanies decrease of 27 %. This is almost the same as the obtained value. The reaction also causes the volume reduction by 27 % and 32 % for formation of $Y_3Al_5O_{12}$ and $YAlO_3$, respectively, based on the density of Y_2O_3, $Y_3Al_5O_{12}$, and $YAlO_3$ being 5,03; 5,35 and 4,55 g/cm³, respectively and molecular weight. This large decrease in 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.

3.3. Reaction of MgO ceramic with molten Al

MgO ceramic also expects to have strong resistance against reduction in molten aluminium. After the reduction test the sample within the alumina tube was cut and polished. Fig. 6 shows photographs and a schematic drawing of it. The outer side of the MgO ceramic became dark gray to black and the thickness was about 0,9 mm. Observation by optical microscope shows that 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 the 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 is simply considered as next equations:

$$4MgO + 2Al \rightarrow MgAl_2O_4 + 3Mg \quad (3)$$
$$K = (a_{Mg})^3/(a_{Al})^2$$

where a_{Mg} and a_{Al} are activities of Al and Mg in the molten aluminium. That of MgO and $MgAl_2O_4$ is considered to be unity, though spinel may form solid solution. Since $\Delta_r G°$ of the reaction (3) is calculated to be 66 kJ at 1298 K, next equations are derived at the equilibrium:

$$\Delta_r G = \Delta_r G° + RT \ln K = 0,$$
then
$$66 \text{ kJ} = -RT \ln (a_{Mg})^3/(a_{Al})^2$$
and
$$(a_{Mg})^3/(a_{Al})^2 = 0,0022$$

If activity of the components is assumed to be equal to their molar fractions in the liquid, $(a_{Mg})^3/(a_{Al})^2 = 0,00223$ when $a_{Mg} = 0,12$. The value seems not so difficult to be achieved. Results of SEM and EDX analysis at the interface between Al and spinel layer are 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 aluminium,
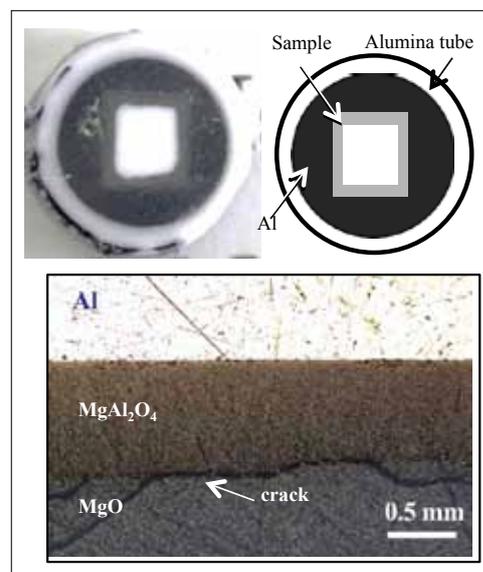
Fig. 6 Cut and polished section of MgO–Al reaction test; upper left: photo, upper right: schematic drawing, lower: optical micrograph


Fig. 7 Crushed MgO pellet after the reduction test

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.

The aluminium after the reduction test was treated with aq. NaOH and the residual was examined by XRD and shown in Fig. 9. Crystalline phase of $Mg_2Al(OH)_7$ is detected besides $Al(OH)_3$. This also confirmed that metallic Mg was dissolving into molten aluminium from MgO pellet.

Spinel layer is also formed on the surface of the alumina tube, as shown in Fig. 10. On the surface of alumina tube, the formation of spinel follows next equation:

$$4Al_2O_3 + 3Mg \rightarrow 3MgAl_2O_4 + 2Al \quad (4)$$
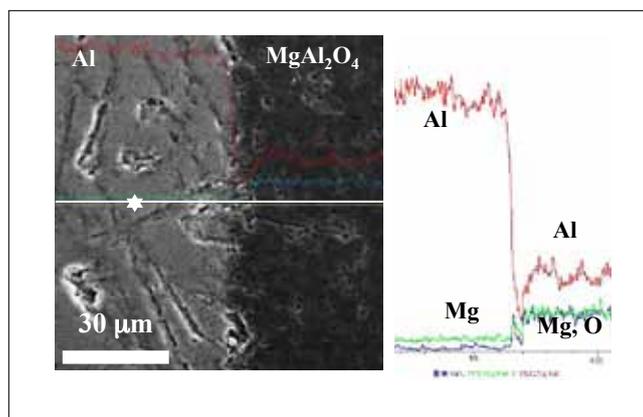
Fig. 8 SEM and EDX measurement of MgO-molten Al interface after reaction at 1000 °C for 25 h
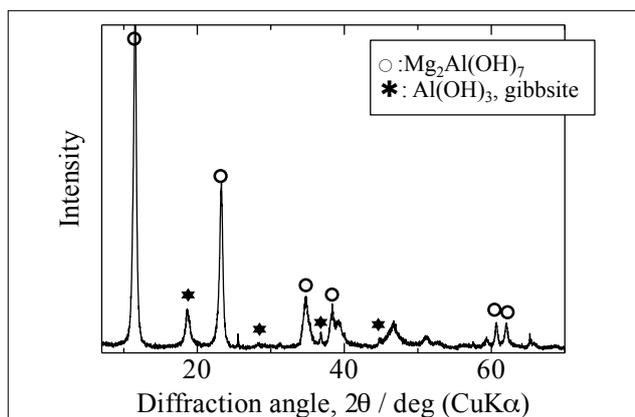
Fig. 9 XRD profile of sediment by treatment with aq. NaOH after reaction of MgO-molten Al. Not marked peaks are not identified

$\Delta_r G°$ of the reaction (4) is −258 kJ at 1298 K and this reaction is favourable. One can see the formation of spinel by two "half reactions" on MgO side (3) and alumina side (4). The thickness of spinel on alumina tube is about 80 μm. Amount of spinel phase formed on the MgO pellet and alumina tube (inner diameter of 12 mm) were roughly estimated as 160 and 200 mm³, respectively. Amount of spinel on Al_2O_3 side was larger and it agrees with the many results of spinel formation experiment using diffusion couple of Al_2O_3 and MgO [7]. When 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 in formed spinel layer. The thickness of spinel is about 500 μm around 1500 °C and soaking for 100–200 h. The thickness ratio of spinel on MgO side and corundum side is 1:3 to 1:4, corundum side is thick.

Comparing the data of the solid state reaction with the present case, thickness of the formed spinel on MgO is quite large, about 0,9 mm at 1000 °C for 25 h. In general reactions, existence of liquid phase may enhance the reaction rate. The present spinel formation reaction, however, is controlled by diffusion of cations through the spinel layer and this diffusion seems independent on the circumstance, whether liquid phase exists or not. The important aspect of present reaction is that spinel formation area on alumina side (inner surface of the tube) is quite larger than the MgO surface. It leads thin spinel layer on alumina tube, but larger amount of spinel. In the usual solid state reaction by diffusion couple, diffusion of
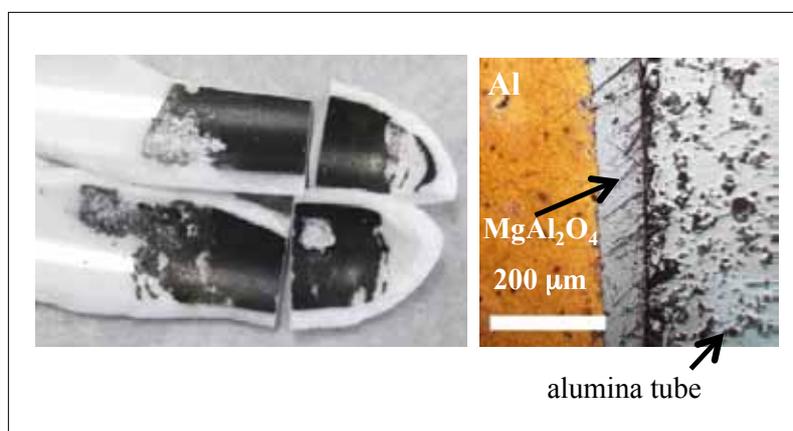
Fig. 10 Alumina tube after the reaction test

cations through spinel on corundum side need a three to four times longer distance. On the contrary, in the present reaction diffusion distance on alumina side should be shorter, because the reaction area is large. This would be a reason why spinel layer formed on MgO pellet is so large.

Another interesting feature on the present spinel formation is the formed spinel is dark gray to black. It suggests that the spinel contained many defects to accelerate ion diffusion. Concerning the protection layer against molten aluminium in former investigations [1, 2], the spinel layer was formed on the surface of Al_2TiO_5 ceramics and this layer prevented the further corrosion. But for the present MgO pellet it is not the case. This is because there is too much MgO to form spinel in the present case.

4 Conclusion

Reaction of TiO_2, $Y_2Ti_2O_7$, Y_2O_3 and MgO with molten aluminium at 1000 °C was investigated. Degree of reaction doesn't depend on the stability of the oxides against reduction. On the surface of TiO_2 and $Y_2Ti_2O_7$ ceramics, formed corundum layer prevents further reaction and Ti^{4+} is not reduced severely. Y_2O_3 pellet reacted with molten Al and, $Y_3Al_5O_{12}$ and $YAlO_3$ formed. This reaction proceeds the entire pellet, because of the decrease in volume by the formation reaction of $Y_3Al_5O_{12}$ and/or $YAlO_3$. The reduced metallic Y dissolved into molten Al and intermetallic compound precipitated during cooling. Spinel formation reaction in the system MgO–Al was very fast comparing the usual solid state reaction. The very high rate of spinel formation and cracks at the interface between formed spinel and MgO made MgO ceramic to be not suitable for refractory for molten aluminium. Among the examined samples, TiO_2 based ceramics had the best performance for the used of refractory for molten aluminium.

References

[1] Yamamoto, S.; et al.: Corrosion of aluminium titanate ceramics by molten aluminium. J. Tech. Assoc. Refractories Jpn. **30** (2010) [3] 162–167

[2] Tanaka, M.; et al.: Effect of grain boundary cracks on the corrosion behaviour of aluminium titanate ceramics in a molten aluminium alloy. Corrosion Sci. **54** (2012) 90–96

[3] Kato, E.; Daimon, K.; Takahashi, J.: Decomposition temperature of β-Al_2TiO_5. J. Amer. Ceram. Soc. **70** (1987) 33–37

[4] Barzilai, S.; et al.: Interface phenomena in the Y_2O_3/(Al–Cu) system. Mater Sci Engin. **A420** (2006) 291–295

[5] Wojewoda-Budka, J.; Sobczak, N.; Morgiel, J.: Interactions between molten aluminium and Y_2O_3 studies with TEM techniques. J. Microscopy **237** (2010) [3] 253–257

[6] Wojewoda-Budka, J.; et al.: Interaction between liquid aluminium and yttria substrate: microstructure characterization and thermodynamic considerations. J. Mater. Sci. **45** (2010) 2042–2050

[7] Yamaguchi, G.: Reactivity of solids. Chap 5. Kagaku Sosetsu 9. Chem. Soc. Jpn. Tokyo 1975 (in Japanese)