Equilibrium Phase Diagram of Mg-Ti-O System (High Titanium Oxide Part) III*

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Abstract

In the previous paper, the authors noted the existence of the eutectics α (TiO_2 solid solution) + β (Ti_2O_3 solid solution) phases and $\beta + \tau$ (Ti_2O_3 solid solution) in the system TiO_2 - Ti_2O_3 . It was also found that the ϵ phase ($\text{MgO} \cdot 2\text{TiO}_2$ solid solution) dissolves large amount of β phase and the domain of this phase seems to extend to the point (composition) at which the atomic ratio of Ti/Mg is nearly 10, and the ϵ phase makes eutectic with the β phase.

In this paper, phase relations of these phases in the ternary system TiO_2 - Ti_2O_3 - MgO (a part of Mg-Ti-O system) estimated by further experiments are described.

Fig. 1 Schematic representation of apparatus for melting point measurement.

Fig. 2 Phase boundary diagram of Mg-Ti-O system (high titanium oxide part).

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Samples were prepared by arc melting of mixtures of chemically pure oxides and sponge titanium with tungsten electrode in argon gas by the apparatus shown in the previous paper. Microscopic observation, x-ray and chemical analysis were carried out for these samples.

The melting points of these samples were also measured by the apparatus shown in Fig. 1, in which samples were heated on molybdenum foil in vacuum or argon gas.

A. Domain of γ solid solution.

1. Samples marked by in Fig. 2 are consisted of the γ single phase. Photo 1 and 2 are their microphotographs. The γ phase is reddish purple and brittle, being hardly etched by HF solution.

Photo. 1 Microphotograph of γ single phase sample (Mg 7.2 atomic %)

Photo. 2 Microphotograph of γ single phase sample (Mg 14.5 atomic %)

2. The crystal lattice of the γ phase is hexagonal, and the lattice parameters a_0 and c_0 change nearly linearly with atomic ratio of Ti/Mg. The single phase domain of the γ phase seems to extend towards MgTiO_3 as shown in Table 1 and Fig. 6.

Table 1 X-ray Analysis of γ Single Phase Samples

Mg/Ti Atomic ratio	0		0.04		0.12		0.18		0.29		0.33		0.40		0.51	
Miller index	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$
(102)	1.00	3.74	1.00	3.74	1.00	3.74	1.00	3.74	0.90	3.74	0.75	3.74	0.65	3.74	0.55	3.72
(014)	0.55	2.71	0.75	2.71	0.85	2.72	0.95	2.72	1.00	2.72	0.90	2.72	1.00	2.72	1.00	2.72
(110)	0.55	2.59	0.65	2.57	0.70	2.57	0.90	2.56	0.70	2.56	0.80	2.56	0.70	2.56	0.55	2.54
(113)	0.30	2.24	0.45	2.24	0.45	2.24	0.70	2.24	0.65	2.24	0.55	2.23	0.55	2.23	0.40	2.23
(204)	0.50	1.870	0.65	1.866	0.55	1.866	0.55	1.866	0.60	1.863	0.55	1.863	0.55	1.863	0.30	1.859
(116)	0.55	1.707	0.80	1.707	0.80	1.710	1.00	1.710	0.95	1.710	1.00	1.710	0.75	1.710	0.60	1.710
(124)	0.25	1.514	0.20	1.512	0.35	1.510	0.40	1.510	0.40	1.508	0.40	1.506	0.35	1.503	0.20	1.501
(300)	0.25	1.488	0.35	1.484	0.45	1.482	0.40	1.480	0.45	1.478	0.45	1.475	0.45	1.473	0.02	1.471
a_0	5.15		5.14		5.13		5.13		5.12		5.11		5.10		5.10	
c_0	13.7		13.8		13.8		13.8		13.8		13.8		13.8		13.8	

B. Domains consisting of two phases.

Photo. 3 Microphotograph of the sample marked by $\oplus$ in Fig. 2; primary crystal ϵ , and eutectic $\epsilon + \alpha$ phase.

Photo. 4 Microphotograph of the sample marked by $\otimes$ in Fig. 2; primary crystal α , and eutectic $\alpha + \epsilon$.

Photo. 5 Microphotograph of the sample marked by $\bigcirc$ in Fig. 2; $\epsilon + \alpha$ eutectic mixture.

1. Samples marked by $\oplus$, $\bigcirc$ and $\otimes$ in Fig. 2 consist of $\alpha + \epsilon$ two phases. Photo 3 is an example of the microphotograph of the sample marked by $\oplus$, in which ϵ primary crystal and $\epsilon + \alpha$ eutectic are observable. In Photo. 4, α phase (bright) is primary crystal and in Photo 5 both crystals seem to be precipitated simultaneously.

Photo. 6 Microphotograph of the sample marked by $\boxplus$ in Fig. 2; primary crystal ϵ , and eutectic $\epsilon + \gamma$.

Photo. 7 Microphotograph of the sample marked by $\boxtimes$ in Fig. 2; primary crystal γ , and eutectic $\gamma + \epsilon$.

2. Samples $\boxplus$, $\square$ and $\boxtimes$ in Fig. 2 consists of $\epsilon + \gamma$ two phases and from this observation the domain of $\epsilon + \gamma$ phase is estimated. In Photo. 6 the ϵ phase is primary crystal, while in Photo 7 the γ phase is primary. ϵ and γ phases crystallise by eutectic reaction.

3. As reported in the previous paper, three eutectics $\alpha + \beta$, $\beta + \gamma$ and $\epsilon + \beta$ are observable and their domains are shown in Fig. 2.

C. Domain consisting of three phases.

1. Samples ∇ in Fig. 2 consists of $\alpha + \beta + \epsilon$ three phases. As shown in Photo 8 the α phase is bright, the β phase is golden yellow and the ϵ phase is grayish blue. The β phase is bright even

Photo. 8 Microphotograph of the sample marked by ∇ in Fig 2; $\alpha + \beta + \epsilon$ phases.

Photo. 9 Microphotograph of the same sample in Photo. 8 under polarized light.

Photo. 10 Microphotograph of the $\alpha+\beta+\epsilon$ phase sample. The parallel cleavage is observable in β phase when etched by HF solution.

Photo. 11 Microphotograph of the sample marked by Δ in Fig. 2; $\beta+\gamma+\epsilon$ phases.

Table 2 Melting Point of the Samples in
Mg-Ti-O System.

Composition atomic %			Melting point °C	Crystalline phase
Mg	Ti	O		
—	34.8	65.2	1730	α
—	35.5	64.5	1680	α
—	36.2	63.8	1610	$\alpha+\beta$
—	36.8	63.2	1650	$\alpha+\beta$
—	37.6	62.4	1690	β
—	38.2	61.8	1640	$\beta+\gamma$
—	38.8	61.2	1680	$\beta+\gamma$
—	39.5	60.5	1750	$\beta+\gamma$
—	40.0	60.0	1820	γ
0.6	37.1	62.3	1680	$\beta+\epsilon$
2.3	35.2	62.5	1600	$\beta+\epsilon$
7.0	31.5	62.5	1620	ϵ
9.2	28.4	62.4	1630	ϵ
10.7	26.8	62.5	1640	ϵ
10.9	27.2	61.9	1640	ϵ
11.1	27.6	61.3	1620	$\epsilon+\gamma$
11.4	28.5	60.2	1610	$\epsilon+\gamma$
11.7	29.2	59.1	1610	$\epsilon+\gamma$
12.0	30.0	58.0	1620	$\epsilon+\gamma$
12.4	31.0	56.6	1620	γ
7.4	29.7	62.9	1630	$\alpha+\epsilon$
7.7	30.6	61.7	1630	$\epsilon+\gamma$
7.9	31.6	60.5	1600	$\epsilon+\gamma$
8.1	32.5	59.4	1610	$\epsilon+\gamma$
8.3	33.4	58.3	1620	$\epsilon+\gamma$
8.6	34.2	57.3	1620	γ
3.9	31.4	64.7	1600	$\alpha+\epsilon$
4.0	32.1	63.9	1600	$\alpha+\epsilon$
4.1	32.5	63.4	1610	$\alpha+\epsilon$
4.2	33.7	62.1	1610	$\epsilon+\gamma$
4.3	34.9	60.8	1590	$\epsilon+\gamma$
4.4	35.8	59.8	1610	$\epsilon+\gamma$
4.6	36.8	58.6	1620	γ
0.5	33.7	65.8	1700	$\alpha+\epsilon$
0.8	34.9	64.3	1650	$\alpha+\epsilon$
0.8	36.3	62.9	1600	$\alpha+\epsilon+\beta$
0.9	37.5	61.6	1610	$\beta+\epsilon+\gamma$
0.9	38.7	60.4	1640	$\beta+\gamma$
0.9	40.0	59.1	1710	γ
1.9	32.8	65.3	1650	$\alpha+\epsilon$
1.6	38.7	59.7	1650	$\beta+\gamma$
9.9	30.1	60.0	1600	$\epsilon+\gamma$

Fig. 3 Phase diagram of $\text{TiO}_2\text{-Ti}_2\text{O}_3$ system.

Fig. 4 Phase diagram of $\text{MgO}\cdot 2\text{TiO}_2\text{-Ti}_3\text{O}_5$ system.

Fig. 5 Phase diagram of Mg-Ti-O system. (high titanium oxide part) (liquidus surface)

under the cross-polarized light as shown in Photo 9. In Photo. 10 characteristic parallel cleavage lines in the β phase, which is produced by deep etching with HF solution, are shown.

2. Samples ∇ in Fig. 2 consist of $\beta + \gamma + \epsilon$ three phases, and the domain of these three phases are estimated roughly from the observations. Photo 11 is a microphotograph of this three-phases sample. The γ phase is easily identified by its reddish purple color.

D. Liquidus surface.

1. Melting points and phases observed are listed in Table 2.

2. Fig. 3 is the equilibrium phase diagram of the TiO_2 - Ti_2O_3 system supposed from the above mentioned observations. The melting point of Ti_2O_3 is 1690°C , and that of TiO_2 is about 1820°C . The eutectic composition of $\alpha + \beta$ eutectic is Ti 36.2, O 63.8 at. %, and that of $\beta + \gamma$ eutectic is Ti 38.5, O 61.5 at. %. The eutectic temperature of the former is estimated to be 1610°C , while that of the latter is 1620°C .

3. Fig. 4 is the equilibrium phase diagram of the $\text{MgO} \cdot 2\text{TiO}_2$ - Ti_2O_3 system. The eutectic composition of ϵ and β phases is Mg 1.5, Ti 36.0, O 62.5 at. %, and the eutectic temperature is about 1600°C .

4. The liquidus surface of the ternary system is shown by isothermal lines in Fig. 5. Estimated binary eutectic lines $\alpha + \beta$, $\alpha + \epsilon$, $\beta + \epsilon$, $\epsilon + \gamma$ and $\beta + \gamma$ phases are shown also in the figure.

5. The composition of $\alpha + \beta + \epsilon$ ternary eutectic is about Mg 1.5, Ti 35.5, O 63.0 at. %, and that of $\beta + \gamma + \epsilon$ ternary eutectic is about Mg 2.0, Ti 37.0, O 61.0 at. %. The eutectic temperature of the former is estimated to be about 1570°C , and that of the latter 1550°C .

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Fig. 6 Relation between Mg/Ti atomic ratio and lattice constant of γ single phase samples.