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A Fundamental Study on Preparation of Al_3Ti Powders by Calciothermic Reduction of Oxides

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The fine Al_3Ti compound powders were produced directly from the oxide mixtures of TiO_2 and Al_2O_3 by the calciothermic reduction using CaH_2. This procedure consists of three steps: raw oxide blending, co-reduction and leaching. After the reduction of the oxide mixture with various compositions, $CaAl_2$ and $Ca_{12}Al_{14}O_{33}$ were often formed as the by-product and transient oxide, respectively. They were removed by leaching in the acid aqueous solution. The obtained Al_3Ti powders was a few micrometer in particle size and contained about 2500 mass ppm oxygen.

The isothermal annealing of the specimens in the Ti-Al-Ca system at 1273 K showed that Al_3Ti is in equilibrium with $CaAl_2$ and the Al-rich Al-Ca liquid at 1273 K. Based on these experimental phase equilibria and on the thermodynamical data in Al-Ca system, the activities of Ca and Al and the phase diagrams at 1273 K were evaluated and revised. By using them the suitable compositions and conditions for the co-reduction were discussed and proposed.

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Keywords: *Al_3Ti, co-reduction, $CaAl_2$, oxide mixture, phase diagram, calciothermic reduction, calcium-titanium-aluminum-oxygen*

I. Introduction

For the industrial materials, the three kinds of titanium-aluminum intermetallic compounds, Ti_3Al, TiAl and $TiAl_3$, have become of extensive interest. Because of their poor ductility, the clean and fine powders are required for the powder metallurgy of these compounds. Our previous studies[1][2] showed that co-reduction of oxide mixtures using metallic calcium can produce the fine Ti_3Al and TiAl powders suitable for the powder metallurgy, since calciothermic reduction of oxides produces alloy powders at low temperatures without melting[3][4]. For the preparation of Al_3Ti single phase by the calciothermic reduction, however, the mingling of Al_2Ti and $CaAl_2$ was predicted on the basis of the calculated phase equilibria in the system Ti-Al-Ca-O[3].

The purpose of this work is to establish experimentally the practical processes to prepare the fine Al_3Ti compound powders by the calciothermic reduction. The chemical reaction to produce Al_3Ti from oxides can be described by the equations:

$$2TiO_2+3Al_2O_3+13Ca=2Al_3Ti+13CaO \quad (1)$$

CaH_2 is available for the reduction of TiO_2 and Al_2O_3 and has been used to produce rare earth magnets[5][6], Ti_3Al[2] and TiAl[1][2] by the co-reduction. We reported[2] that the hydrogen due to calcium hydride did not affect any reactions in the Ti-Al system and obtained that CaH_2 was more effective than metallic calcium for the reduction of TiO_2. These reactions are characterized by starting from easily available oxides, but there are some difficulties related to (1) removal of oxygen, (2) single phase preparation, and (3) stoichiometry control of the compounds[1]-[3][7]. Titanium and calcium are mutually insoluble[8], while calcium and aluminum may form a liquid alloy or $CaAl_2$ compound at the reduction temperatures[9]. If Al_3Ti is in equilibrium with $CaAl_2$ as predicted previously[3], therefore, the adequate process should be developed to obtain the Al_3Ti single phase by the calciothermic reduction.

In our previous reports[2][3], the existence of Al_2Ti was neglected for the calculation of phase diagram of the Ti-Al-Ca-O system. Furthermore, there is a doubt about the calculated phase equilibria among $CaAl_2$, Al-rich Al-Ca liquid and the complex oxides in the Ca-Al-O system. This paper also deals with the experimental results on the phase equilibria in the Al-rich Ti-Al-Ca system, directing towards the production of Al_3Ti single phase.

II. Experimental Procedure

Al_3Ti was formed by reducing the mixture of TiO_2 and Al_2O_3 with calcium hydride as a reducing agent. Figure 1 represents the procedure of this work; raw material blending, high temperature reaction and acid leaching for removal of the by-products.

For the preparation of oxide mixture, rutile and α-alumina powder were mixed in a desired ratio using an agate mortar. The particle sizes of high purity TiO_2 and Al_2O_3 used here were in the order of submicrons. CaH_2 used in this study was of about 98% purity: CaO was the main impurity. The CaH_2 powder was mixed with the oxide mixture blended in advance.

The experimental apparatus and method for the reduction experiments were similar to those described previously[1][2][7][10]. About 1g of the premixed powder sample was placed on the molybdenum tray, and they were tightly

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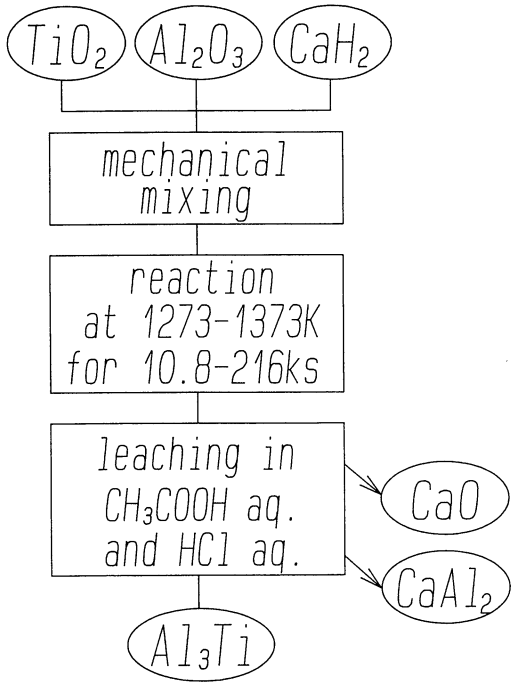

Fig. 1 Experimental procedure.

covered with a stainless steel cap and a bottom plate. Considering the vapor pressure of calcium[2], the vessel was sealed by a small amount of liquid calcium to avoid the leakage of the reductant. After a given holding time in the purified argon atmosphere at 1273 or 1373 K, the vessel was cooled in the furnace.

The reduction products containing the desired compound, CaO and the residual reducing agent often formed a gray-colored hard cake with about 10 mm in diameter and about 3 mm thick. They were crushed and slurried in a CH_3COOH aqueous solution (pH=3). The successive leaching with a 1 kmol·m^{-3} HCl aqueous solution was done with supersonic vibrations. The centrifugated compound powders were rinsed with distilled water, alcohol and acetone, then dried in a vacuum.

To check the phase equilibria in Ti-Al-Ca system, about 2 g of the samples with the various compositions were annealed in a tantalum crucible for 2 d at 1273 K in the stainless steel tubes which were sealed at both ends by welding in argon gas. The starting materials were pure titanium powder (1200 mass ppm oxygen), 99.5% aluminum powder and high purity calcium lumps. Al_2Ti and $CaAl_2$ prepared in advance were also used in addition to TiAl powder produced by plasma rotating electrode process and Al_3Ti polycrystals by HIP.

The identification of the phases existing in the samples was carried out by X-ray diffractometry using a Philips PW1700 system, and the results were compared with JCPDS cards and the reported data of Al_2Ti[11]. X-ray microprobe analysis (XMA, Hitachi X-650) was done to obtain the compositional profiles. The morphology and configuration of the powder were examined by scanning electron microscopy (SEM, Hitachi S-450). A LECO TC336 analyzer was used for oxygen analysis. Aluminum and calcium were chemically analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Nippon Jarrell-Ash ICAP-575II).

III. Results

1. Preparation of Al_3Ti

Figure 2 shows X-ray diffraction (XRD) patterns of the sample reduced by CaH_2 at 1273 K for 10.8 ks. The starting material was the oxide mixture containing Al_2O_3 and TiO_2 with a Al/Ti ratio of 3/1. The pattern (a) shows that the sample after the reduction contained CaO and $Ca(OH)_2$ as the major phases. $Ca(OH)_2$ was formed by the reaction of CaO with the atmospheric moisture during handling before XRD measurement. The metallic calcium and CaH_2 were hardly detected by X-ray diffraction for all the specimens studied here. CaO and $Ca(OH)_2$ were easily removed by CH_3COOH aq. as shown in Fig. 2(b), where the existence of $CaAl_2$ and Al_2Ti in addition to Al_3Ti is more clearly seen than in Fig. 2(a). The by-product, $CaAl_2$, could be completely separated after leaching by HCl aqueous solution. The powder containing Al_3Ti and Al_2Ti was obtained as shown in Fig. 2(c).

When the stoichiometric amount of CaH_2 was used for the reduction of the oxide mixture containing Ti and Al

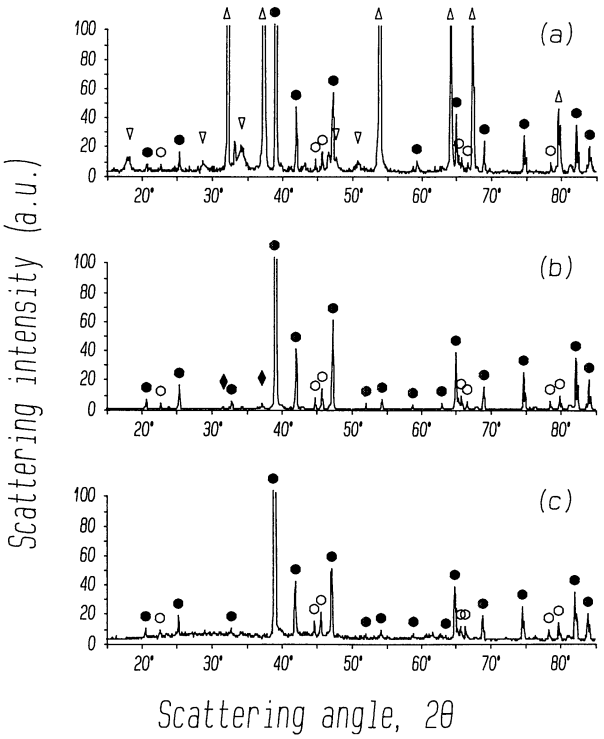

Fig. 2 XRD patterns using CuK_α for the sample reduced at 1273 K for 10.8 ks from the oxide mixture with a ratio of Al/Ti=3/1. Pattern (a) was for the as-reduced specimen. (b) was for the same specimen after leaching in CH_3COOH aqueous solution. (c) was for the same specimen after the subsequent leaching in HCl aq. The symbols in the figure indicate CaO(△), $Ca(OH)_2$(▽), $CaAl_2$(◆), Al_2Ti(○) and Al_3Ti(●).

at the ratio of 1:3, a large amount of complex oxides in the Ca-Al-O system was produced in addition to Al_3Ti even after the reduction time longer than 10 ks at 1273 K. The amount of reductant was, therefore, increased to 1.2 times the stoichiometric amount as shown in Fig. 2. The complex oxides such as $Ca_{12}Al_{14}O_{33}$ could not be detected in this case, but the by-product, $CaAl_2$, was formed by the excess amount of calcium. Al_2Ti and $CaAl_2$ were preferentially produced in addition to Al_3Ti, both when the excessive amount of CaH_2 was used and when the reduction time was made longer than 10 ks at 1273 K. The similar results have already been reported in the preparation of TiAl[2][7].

It was thought that the formation of $CaAl_2$ decreased aluminum concentration of Al-Ti alloy in the sample, and that Al_2Ti was, therefore, formed in addition to Al_3Ti. It was needed to increase the Al/Ti ratio in the oxide mixture larger than 3/1 in order to compensate the aluminum loss. The excess amount of CaH_2 was needed both for the complete reduction of oxides and for the lack of calcium due to a small amount of leakage from the vessel. An airtight vessel, for example, sealed by welding, may give a better result. In this study CaH_2 as much as 1.2 to 1.8 times its stoichiometric amount was normally used for the reduction.

Table 1 summarizes the results of the phase identification by XRD measurements and XMA for the samples reduced from the oxide mixtures with various compositions. At the lower aluminum concentration than 75 mol%Al, TiAl or Al_3Ti was produced in addition to Al_2Ti. The formation of these two phase mixtures can be generally understood on the base of the phase diagram in Ti-Al binary system[12], although a small amount of $CaAl_2$ and $Ca_3Al_2O_6$ coexisted.

At the aluminum concentration range between 80 and 90 mol%Al, Al_3Ti was obtained as the prevailing phase in the powders after the reduction at 1273 K for 10.8 ks. The samples in these compositions contained CaO, $CaAl_2$ and a very small amount of $Ca_{12}Al_{14}O_{33}$ as by-products of the reduction, and they could be separated by leaching. The scanning electron micrograph in Fig. 3

Fig. 3 Scanning electron micrograph of Al_3Ti powders reduced by CaH_2 for 10.8 ks at 1273 K. The molar ratio of Al:Ti in the starting oxide mixture was 85:15.

revealed the morphology of the calciothermic Al_3Ti powder after the reduction of the oxide mixture with a ratio of Al/Ti=85/15. The fine isolated particles could be seen after the removal of CaO and the by-products. This powder contained about 2500 mass ppm oxygen and 350 ppm calcium on the average of three independent runs.

When pure alumina was reduced, as listed in Table 1, CaO, $CaAl_2$ and $Ca_{12}Al_{14}O_{33}$ were formed as the major phases and pure aluminum has rarely detected by the reduction of CaH_2. One of the reasons is that the molybdenum or tantalum plate holding the sample powder partially reacted with the produced aluminum.

In this work, the transient oxides, such as $Ca_3Al_2O_6$ and $Ca_{12}Al_{14}O_{33}$, disappeared after the prolonged reaction period or when the amount of CaH_2 was increased. Under the cases listed in Table 2, there were some

Table 1 The results of the phase identification by XRD measurement and XMA for the samples reduced from the oxide mixtures with various compositions. The co-products were determined for the samples after the reduction at 1273 K for 10.8 ks and also after the subsequent leaching by CH_3COOH aq.

Molar ratio in the oxide mixture Ti:Al	Identified phases	
	Al-Ti alloys	Co-products
35:65	TiAl, Al_2Ti	CaO, $CaAl_2$
30:70	Al_2Ti, Al_3Ti	CaO, $CaAl_2$, $Ca_3Al_2O_6$*
25:75	Al_2Ti, Al_3Ti	CaO, $CaAl_2$
20:80	Al_3Ti	CaO, $CaAl_2$*
15:85	Al_3Ti	CaO, $CaAl_2$, $Ca_{12}Al_{14}O_{33}$*
10:90	Al_3Ti	CaO, $CaAl_2$, $Ca_{12}Al_{14}O_{33}$
0:100	—	CaO, $CaAl_2$, $Ca_{12}Al_{14}O_{33}$

* Minor phase in the specimen.

Table 2 The results of the phase identification by XRD measurement and XMA for the samples reduced from the oxide mixtures with various compositions. The co-products were determined for the samples after the reduction at 1273 K for the period longer than 10.8 ks and also after the subsequent leaching by CH_3COOH aq.

Molar ratio in the oxide mixture Ti:Al	Reduction time (ks)	Identified phases	
		Al-Ti alloys	Co-products
35:65	172.8	TiAl, Al_2Ti	CaO, $CaAl_2$
25:75	86.4	TiAl, Al_2Ti	CaO, $CaAl_2$
20:80	86.4	Al_2Ti	CaO, $CaAl_2$
15:85	86.4	Al_3Ti	CaO, $CaAl_2$
10:90	216	Al_3Ti	CaO, $CaAl_2$

changes in the phases obtained after leaching, compared with the results in Table 1. The phases at the lower aluminum content were generally obtained in the conditions of Table 2. It was also confirmed by the chemical analysis that the aluminum concentration of the powders in the Al-Ti system decreased after the reduction. The reduction at 1373 K gave a similar result to that at 1273 K, as described above.

2. Ti-Al-Ca phase diagram

Figure 4 shows the phase diagram in the Ti-Al-Ca system at 1273 K studied by this work. After the identification of the solid phases by XRD measurements, the Ca-Al based alloys were extracted from the annealed specimens by leaching. The analyzed concentrations of Ca-Al liquid were, however, scattered within 10 mol%Al from the expected composition because of the creeping from the crucible and of the reaction with the atmospheric moisture. Both the titanium content in Ca-Al alloys and the calcium in Ti-Al alloys were less than 0.3 mol%. The experimental phase equilibria in Fig. 4 were drawn supposing that the compositions of the liquidus equilibrating with $CaAl_2$ are 58.0 and 76.5 mol%Al as shown in the binary phase diagram[9]. It should be noted that three phase equilibrium among Al_2Ti, Al_3Ti and $CaAl_2$ was confirmed for the specimens which had been brought from pure elements or the intermetallic compounds in a desired composition. The existence of Al_2Ti had been ignored in the previous calculations[2].

IV. Discussion

1. Activities in Ca-Al liquid

Our previous study[2] reported the calculated phase diagram of the Ti-Al-Ca system based on the thermodynamical evaluations from the literatures, where the activities in Ca-Al liquid alloy were extrapolated at 1273 K by the regular solution approximations using only by the data at 1623 K[13]. Jacob *et al.*[14] have recently reported the activities of calcium and aluminum in the liquid Ca-Al alloys at 1373 K. Our previous approximations can not be reasonably explained by their data. Combining the two reports at two temperatures[13][14], the activity coefficients, γ, is expressed by:

$$\ln \gamma = A/T + B \tag{2}$$

where A and B are constants at a given composition, and T is temperature. This equation has been commonly used to express the temperature dependency of the activity coefficients in many alloys. Table 3 shows the activities in Ca-Al liquid alloy at 1273 K, and the values evaluated in this study were found to be larger negative deviations than the previous estimation[2]. Applying this approximation, the standard free energy of $CaAl_2$, ΔG_f° can be evaluated at 1273 K by:

$$Ca(1) + 2Al(1) = CaAl_2(s) \tag{3}$$

$$\Delta G_f^\circ = -RT \ln (a(CaAl_2)/a(Ca)a(Al)^2) \tag{4}$$

where R is gas constant and $a(CaAl_2)$, $a(Ca)$ and $a(Al)$ are the activities of $CaAl_2$, calcium and aluminum, respectively. The results are shown in Table 4 and compared with the previous works[15]-[17]. This result shows that there is a small difference between that in the Al-richer region than $CaAl_2$ and that in the Ca-richer region, and these values differed with the reported values[15]-[17]. There is, however, quite large difference among the reported values, and a further study should be required about $CaAl_2$.

The extrapolated activities in the Ca-Al system were used for the calculation of the phase equilibria and the conjugation lines both in the Ti-Al-Ca and in the Al-Ca-O system. The results are shown in Fig. 4 and Fig. 5, respectively, where the other thermodynamic values are the same as the previous estimation[2]. $Ca_{12}Al_{14}O_{33}$ was thought to be unstable[18] and omitted in Ref. (2) but it is taken into account in Fig. 5 to explain our results on the basis of the thermodynamic data[15][18]. Al_3Ti single phase

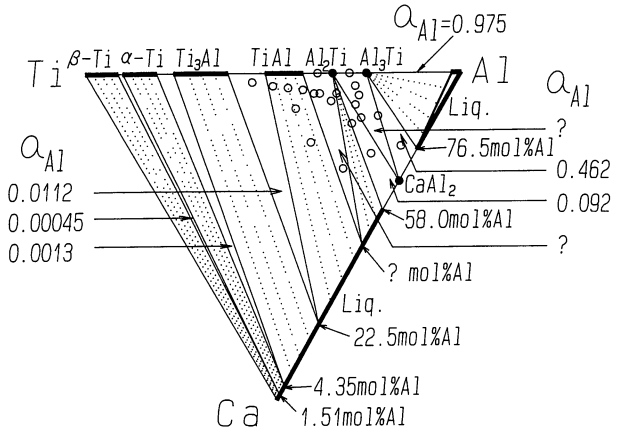

Fig. 4 Phase diagram of ternary system of Ti-Al-Ca at 1273 K. The open circles show the experimental compositions. The phase equilibria were estimated by the phase identification and by the activities extrapolated from Ref. (14) and the literature in Ref. (2).

Table 3 The activities at 1273 K in the Ca-Al system. The values in this study were evaluated on the basis of the reports by Schürmann *et al.*[13] and Jacob *et al.*[14]

Composition	This study		Ref. (2)	
	a(Al)	a(Ca)	a(Al)	a(Ca)
58.0-66.7 mol%Al	0.092	0.139	0.216	0.141
66.7-76.5 mol%Al	0.462	0.008	0.622	0.025

Table 4 Standard free energy of formation of $CaAl_2$.

Reference	ΔG_f° of $CaAl_2$ (kJ/mol)		
	1273 K	823 K	800 K
This work			
58.0-66.7 mol%Al	−67.45		
66.7-76.5 mol%Al	−71.39		
Barin *et al.*[15]	−188.87	−205.92	−206.27
Nortin *et al.*[16]			−91.4±0.2
Veleckis[17]			−86.13

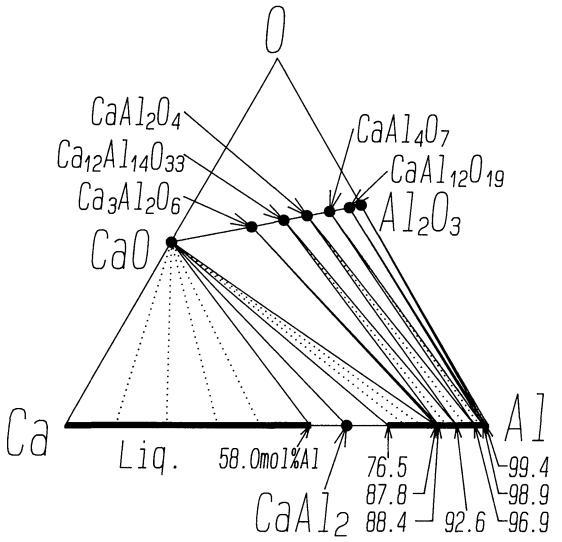

Fig. 5 Phase diagram of the Ca–Al–O system at 1273 K. The phase equilibria were estimated by the oxygen partial pressure and the activities using the previous reports[2][13][14][18].

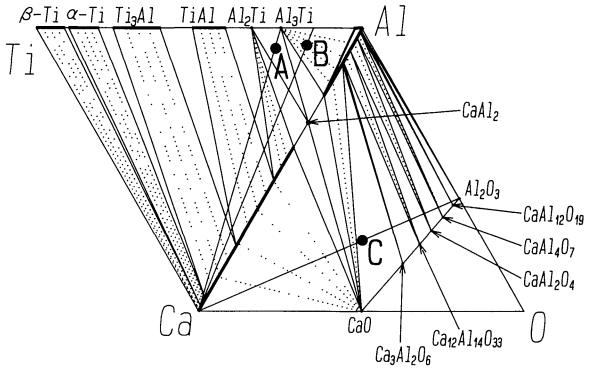

Fig. 6 Explanation of the compositional change in the phase diagrams during the reduction.

can coexist with the liquid aluminum for a wide compositional range between pure aluminum and $CaAl_2$ at 1273 K. It should be noted that CaO can not be in equilibrium with pure aluminum but with the liquid alloy at 87.8 mol%Al at maximum. The compositions of the Ca–Al liquid are still unknown with which Al_2Ti and TiAl are in equilibrium, because there is no thermodynamic information about Al_2Ti and the data by chemical analysis were scattered experimentally.

Jacob *et al.*[14] showed that CaO crucible was not suitable to hold the Al-rich Ca–Al liquid alloys, and they suggested that the complex oxides such as $CaAl_2O_4$ and $Ca_3Al_2O_6$ could be equilibrated with the Al-rich liquid. Their results strongly support the reliability of the calculation in Fig. 5. Figures 4 and 5 may be more accurate than the figures in Ref. (2).

2. Processes of the calciothermic reduction

The phase diagrams are the useful guides to explain the process to prepare Ti_3Al and TiAl by the calciothermic reduction[2][3]. Supposing that Al_2O_3 and TiO_2 are independently reduced to the metallic state and then aluminum and titanium form the intermetallic compound, the phase diagram of the Ti–Al–Ca system gives us some precious informations why $CaAl_2$ was formed as the by-product.

Al_3Ti formed by the calciothermic reduction reacts with the excessive amount of calcium and the total composition of the system shifts from Al_3Ti to the point A in Fig. 6, where Al_2Ti and $CaAl_2$ coexist with Al_3Ti. This is the reason why the mixture of Al_2Ti and Al_3Ti was obtained from the oxide mixture with the compositional ratio of $Al/Ti=3$.

When the initial composition of the starting oxide mixture is controlled to be $Al/Ti>3$, for example, the point B in Fig. 6, the reaction with calcium produce the Al-rich liquid in addition to Al_3Ti. In cooling, the liquid may decompose into the $CaAl_2$ and a small amount of aluminum or $CaAl_4$[9] ($CaAl_4$ is stable below 973 K). The latter two phases, however, were not detected in this study, because they dissolve easily in the acid solution during leaching.

The reduction process of Al_2O_3 are also shown in Fig. 6, where many transient oxides may form on the way to metallic aluminum. If the stoichiometric amount of calcium for the reduction of Al_2O_3 is used (the case "C", in Fig. 6), the obtained phases should consist of three phases, metallic liquid with 87.8 mol%Al, $Ca_3Al_2O_6$ and CaO. The Al–Ca liquid solidifies into $CaAl_4$ and aluminum according to the binary diagram[9]. The coexistence of CaO, $CaAl_2$ and $Ca_{12}Al_{14}O_{33}$ was, however, found in this work. The reduction seems to be done through a non-equilibrium process. For further quantitative discussion to clarify the reduction route, the phase equilibria in the Ti–Al–Ca–O quaternary system are required.

In order to obtain the single phase of Al_3Ti in this stage, the compositional ratio in the oxide mixture and the amount of the reductant are important, because Al_2Ti as the by-product could not be removed by leaching in the acid solution. The oxides should be, therefore, mixed at the molar ratio of $Al/Ti>3$. The excessive amount of the reductant should be minimized so that the total composition may not enter the stable region of Al_2Ti. The quantities of aluminum, titanium and calcium should be, therefore, controlled as the following three mass balance.

$$n_{Al} \geq 3n_{Ti} \tag{5}$$

$$n_{Ca} \geq (3/2)n_{Al} + 2n_{Ti} \tag{6}$$

$$n_{Ca} \leq 2n_{Al} + (1/2)n_{Ti} \tag{7}$$

where n_{Al} and n_{Ti} are the number of moles of aluminum and titanium, respectively. n_{Ca} is the total number of moles from calcium in CaH_2 and that from the sealing material. In this condition, the by-product is only $CaAl_2$ and it can be easily removed by the HCl aqueous solution.

V. Conclusion

The fine Al_3Ti compound powder was produced directly from the oxide mixtures of TiO_2 and Al_2O_3 by calciothermic reduction using CaH_2. This procedure consists of three steps: raw oxide blending, co-reduction and leaching. The transient phases such as $Ca_{12}Al_{14}O_{33}$ and $Ca_3Al_2O_6$ were disappeared by the reaction for longer period than 10 ks at 1273 K. $CaAl_2$ as the by-product could be removed by leaching in the HCl aqueous solution, but Al_2Ti could not.

The phase diagrams were re-evaluated on the base of the recent thermodynamic data[14] and the experimental results in this study. Al_2Ti was stable in the Ti–Al–Ca system at 1273 K. Based on the phase diagrams, the Al_3Ti single phase in this calciothermic process could be produced by the delicate control of the compositions of the oxide mixture and the amount of the reductant.

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