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Preparation of TiAl and Ti_3Al Powders by Calciothermic Reduction of Oxides

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The clean and fine Ti_3Al and TiAl compound powders were produced directly from the oxide mixtures of TiO_2 and Al_2O_3 by the calciothermic reduction using vapor calcium, liquid calcium or CaH_2. This procedure consists of three steps: raw oxide blending, co-reduction and leaching. The history of the preparation of the oxide mixtures had no effect on the production of the powders of a desired composition. The use of CaH_2 powder for the reduction gave better results than that of the other reductants on the oxygen contents in the reduced powders. The indication on stoichiometric control in this procedure is thermodynamically discussed.

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Keywords: *TiAl, Ti_3Al, co-reduction, CaH_2, oxide mixture, calciothermic reduction, Ti-Al alloy, phase diagram*

I. Introduction

In the last ten years, there has been considerable interest in titanium-aluminum intermetallic compounds, Ti_3Al, TiAl and $TiAl_3$, as materials for products, such as engine parts. The consolidated parts made of the alloy powders by HIP- or CIP-vacuum sintering are very useful. Atomizing is one of the effective methods of producing these alloy powders. Another possibility is a novel method of producing TiAl and Ti_3Al powders by calciothermic reduction of oxide mixtures, which is the method examined in this work.

So far the direct compound reduction techniques, called the co-reduction and Reduction-Diffusion (RD) processes, have been successfully used for the preparation of permanent magnetic materials, such as Sm-Co[1)-3)] and Nd-Fe-B[4)5)], and the superconducting Nb_3Sn powders[6)]. Previously the authors briefly reported that Ti-Al alloy powder can be obtained from the mixed oxide by the co-reduction using Ca vapor[7)]. The obtained powder was very fine, since calciothermic reduction of oxides produces alloy powder at low temperatures without melting. The chemical reactions to produce TiAl and Ti_3Al from oxides can be described by the equations:

$$2TiO_2+Al_2O_3+7Ca=2TiAl+7CaO$$

$$6TiO_2+Al_2O_3+15Ca=2Ti_3Al+15CaO$$

CaH_2 is also available for the reduction of TiO_2 and Al_2O_3 because of its strong affinity with oxygen. This has been used to produce Sm-Co and Nd-Fe-B magnets by the co-reduction or RD process[3)8)]. These reactions are characterized by starting from easily available oxides, but there are some difficulties[7)] depending on: (1) removal of oxygen to the level satisfying the commercial standards, (2) single phase preparation, and (3) stoichiometry control of the compounds. It should be noted that titanium and calcium are mutually insoluble[9)], while calcium and aluminum may form a liquid alloy or $CaAl_2$ at the reduction temperature[10)].

Our first report on the calciothermic reaction in Ti-Al system mainly dealt with the preparation of Ti-dilute Al alloys[7)]. This paper reports the results of experimental investigations directed towards the production of clean TiAl and Ti_3Al compounds by the co-reduction process using calcium hydride in addition to calcium.

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II. Experimental Procedure

Two non-stoichiometric phases, Ti_3Al and TiAl, and a stoichiometric $TiAl_3$ are present in the Ti-Al system[11)]. Ti_3Al and TiAl compounds were formed by reducing the mixture of TiO_2 and Al_2O_3 with calcium as the reducing agent. Figure 1 represents the procedure of this work; raw material blending, high temperature reaction and acid leaching for removal of the by-product CaO.

1. Preparation of oxide mixture

For the preparation of oxide mixture, the following three methods were employed in this work:

(1) Co-precipitation from chloride solution

High-purity $TiCl_4$ and $AlCl_3 \cdot 6H_2O$ were dissolved at a desired atomic ratio in concentrated HCl solution. This solution was dropped into aqueous ammonium solution, and the pH of the neutralized solution was controlled between 5 and 7[7)]. After separation of the precipitates from the solution by centrifugation, the ammonium chloride adhering to the precipitates was removed by rinsing several times with distilled water. The white-colored cake of dried precipitate was ground into powder, and calcined at 873 K over night in air to evaporate any NH_4Cl

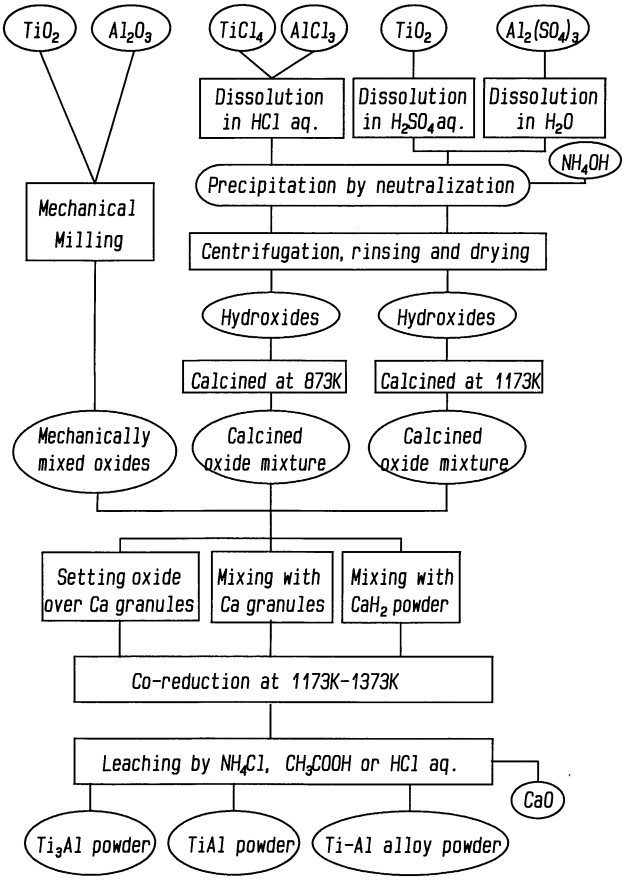


Fig. 1 Experimental procedure.

completely.

(2) Co-precipitation from sulfate solution

TiO_2 was dissolved in H_2SO_4 aqueous solution with $(NH_4)_2SO_4$, and $Al_2(SO_4)_3$ was separately dissolved in water. These blended solutions were added into ammonium solution and the simultaneous precipitates were rinsed, dried and calcined at 1173 K for 10 ks in air.

(3) Mechanical mixing of oxide

The mechanical mixture was prepared by mixing rutile and α-alumina powder 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 sub-microns.

Three possible kinds of reductant (vapor calcium, liquid calcium and solid CaH_2 powder) are applicable to the reduction of oxides. The choice was made after examination of all three cases. Both the calcium and CaH_2 used in this study were of about 98% purity: CaO was the main impurity.

2. Reduction and leaching

The reduction experiments were carried out in a stainless steel vessel. In the case of reduction by calcium saturated vapor, the apparatus and experimental method have been described previously[6][7][12], and only a brief outline will be given here. The reducing agent was put on the bottom of the vessel, and the premixed oxide powder was placed on a molybdenum tray in the vessel. After a given holding time in the purified argon atmosphere at a reduction temperature between 1123 and 1373 K, the vessel was cooled in a furnace. Equilibrium vapor pressure of calcium is evaluated to be 1750 Pa at 1273 K[13]. Special care was taken to avoid the leakage of the reductant from the vessel.

For the reduction by liquid calcium, the calcium metal granules were mixed with the oxide mixture and loaded on a molybdenum tray. For the reduction by CaH_2, 1.2 to 3.0 times the stoichiometric quantities of CaH_2 powder were well blended with the oxide mixture, compacted into a disk and inserted into a reduction vessel lined with molybdenum.

The reduction products containing the desired compound, CaO and the residual reducing agent often formed a hard cake especially when liquid calcium or CaH_2 was used. They were crushed and slurried in 1.53 $mol \cdot kg^{-1}$ NH_4Cl, CH_3COOH (pH=3) or 1 $kmol \cdot m^{-3}$ HCl aqueous solution with supersonic vibration or stirring. The centrifugated compound powders were rinsed with distilled water, alcohol and acetone, then dried in a vacuum.

3. Analysis of obtained compounds

The identification of the phases existing in the specimens was carried out by X-ray diffractometry using a Philips PW1700 system, and the results were compared with JCPDS cards. 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) without etching and without electron-conductive evaporated film. Specimens were analyzed for oxygen and calcium. A LECO TC336 analyzer was used for oxygen analysis, and calcium was chemically analyzed by both atomic absorption spectrometry (SIMADZU AA-670) and inductively coupled plasma-atomic emission spectrometry (ICP-AES, Nippon Jarrell-Ash, ICAP-575II).

III. Results

1. Preparation of Ti_3Al

The calcined precipitates started from the chloride or sulfate were identified as the mixture of TiO_2 and Al_2O_3 by X-ray diffraction measurements. The specimens reduced by calcium vapor or calcium liquid consisted of the desired compound and the by-product, CaO. The excess reducing agent, calcium, also coexisted with them. These results agreed well with our previous work[7]. Figure 2 shows the X-ray diffraction patterns of the samples reduced by CaH_2, where (a) and (b) show the reduction products and the compound powders after leaching, respectively. The metallic calcium was often found after reduction by CaH_2, while CaH_2 was hardly detected by X-ray diffraction measurements. CaO and calcium were easily removed by the wet method. In the case of the powders

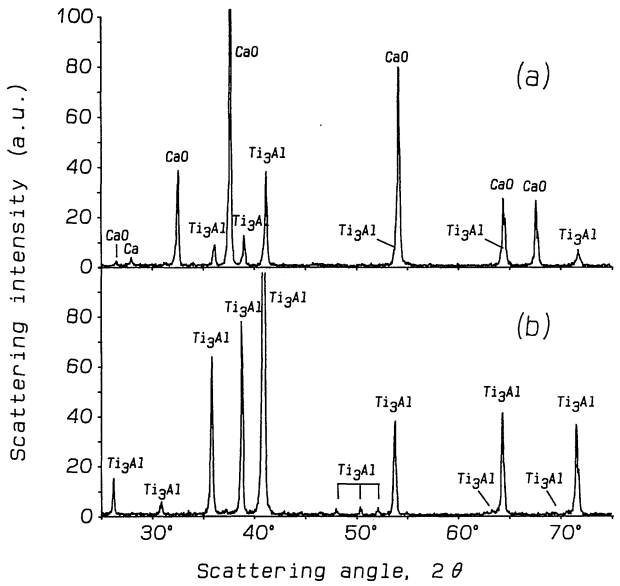


Fig. 2 X-ray diffraction patterns using Cu $K\alpha_1$, of the Ti_3Al powder. The pattern (a) was for the specimen reduced at 1273 K for 43.2 ks by CaH_2, and the pattern (b) was for the same specimen after leaching of the reduced specimen with CH_3COOH aqueous solution.

after leaching, after being reduced by calcium vapor, calcium liquid or CaH_2, X-ray diffraction measurements confirmed that the Ti_3Al single phase existed in all the specimens started from the oxide mixture containing Al_2O_3 and TiO_2 with a Al/Ti ratio of 1/3. From the view of identification of the formed phases, there was no difference between the specimens started from the calcined oxide mixtures and the mechanical oxide mixture. No oxides nor transient phases were detected in the samples reduced for periods longer than 3.6 ks, which was the shortest in this work. Ca–Al alloys as the by-product were never detected after the reduction.

Table 1 summarizes the analyses of Ca and oxygen contents in the reduced Ti_3Al powders. Three leaching solutions, NH_4Cl, CH_3COOH and HCl aqueous solutions, were used to dissolve the by-product CaO and the residual reducing agent, but no significant difference was recognized among them. The analyzed oxygen and calcium level in the Ti_3Al compound powders depended strongly on the experimental conditions. The oxygen contents of the powders reduced by vapor calcium or liquid calcium were about 2500–4000 mass ppm, which was higher than those by CaH_2 (about 1200–3000 ppm). From 73 independent experiments we obtained the lowest contents of oxygen and calcium as 1200 mass ppm and 180 mass ppm, respectively.

To clarify the effect of the oxygen dissolved in the leaching solution, argon gas, air or pure oxygen gas was blown into the CH_3COOH solution before and during leaching. As seen in Table 2 three kinds of gases gave similar results. Stirring the solution by gas bubbling might have an effect on impurity elimination on the surface of the reduced powder.

The scanning electron micrographs in Figs. 3–5 revealed the morphology of the calciothermic Ti_3Al powders. The fine isolated particles could be seen after the removal of CaO. The particle size depended significantly on the reducing temperature, the reducing period and the reductant, but not on the history of the starting oxide mixture. The reduced powders were found to have a tendency to be sintered at higher temperatures or for longer periods, and to decrease their oxygen contents.

Titanium and aluminum atoms in the reduced powder were dispersed homogeneously within the limit of resolution of XMA. We could not detect any traces of chlorine or sulfur in the reduced specimens, which might have come from the starting chloride or sulfate[7]. Since the chemically analyzed aluminum concentration of the reduced Ti_3Al powder corresponded to the nominal content (25 mol%Al) within the experimental error(± 2 mol%), as will be mentioned later, we concluded that the obtained powder consisted of homogeneous Ti_3Al intermetallic compound with the desired composition.

2. Preparation of hexagonal solid solution

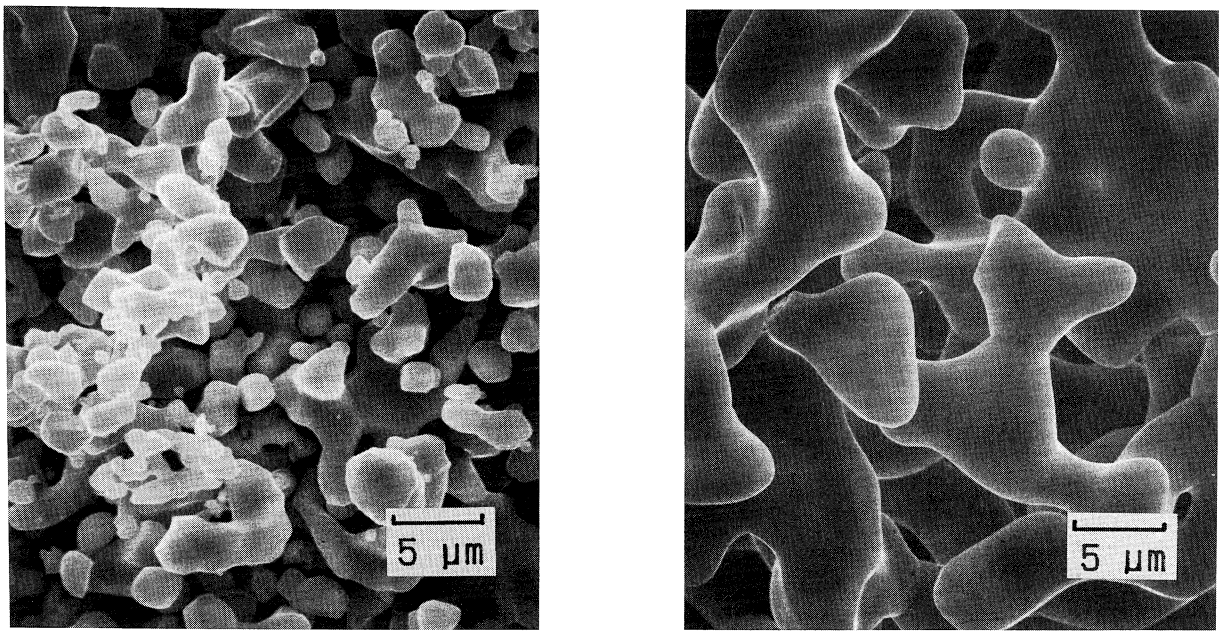
After leaching, X-ray diffraction measurements for Ti–0 to 40 mol%Al powders confirmed that the hexagonal phase (α-Ti and Ti_3Al) existed in all the samples reduced

Table 1 Results of chemical analyses of oxygen and calcium in the Ti_3Al specimens after being reduced by CaH_2 and following leaching by NH_4Cl, CH_3COOH and HCl aqueous solutions.

Reducing condition	Leaching solution		
	CH_3COOH aq.	HCl aq.	NH_4Cl aq.
1223 K 86.4 ks	4600 ppm O 1000 ppm Ca	4300 ppm O 990 ppm Ca	5600 ppm O 930 ppm Ca
1273 K 21.6 ks	2900 ppm O 830 ppm Ca	3100 ppm O 1000 ppm Ca	—
1273 K 21.6 ks	2500 ppm O 230 ppm Ca	2500 ppm O 270 ppm Ca	—
1273 K 21.6 ks	2200 ppm O 220 ppm Ca	3500 ppm O 180 ppm Ca	—
1323 K 43.2 ks	1600 ppm O 2300 ppm Ca	—	1200 ppm O 630 ppm Ca

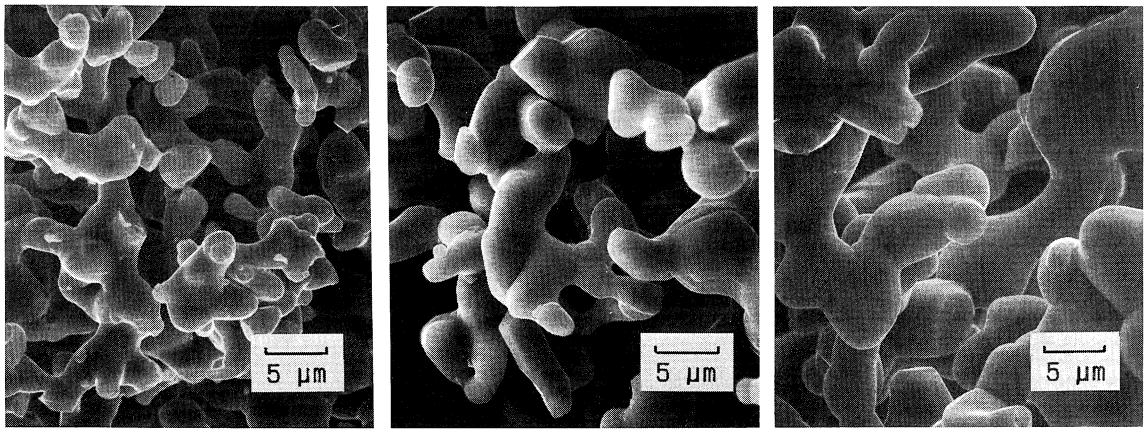
Table 2 Results of chemical analyses of oxygen and calcium in the Ti_3Al specimens after being reduced by CaH_2 and following leaching by CH_3COOH aqueous solutions for 14.4 ks, where argon gas, oxygen gas or air was blown into the solutions before and during leaching.

Reducing condition	Leaching solution			
	Ar bubbling	Non bubbling	Air bubbling	O_2 bubbling
1223 K 43.2 ks	5400 ppm O 940 ppm Ca	5800 ppm O 1000 ppm Ca	5900 ppm O 1000 ppm Ca	—
1273 K 21.6 ks	2900 ppm O 790 ppm Ca	3700 ppm O 900 ppm Ca	—	—
1323 K 86.4 ks	2400 ppm O 300 ppm Ca	2200 ppm O 450 ppm Ca	—	2300 ppm O 340 ppm Ca
1323 K 43.2 ks	2200 ppm O 390 ppm Ca	—	—	200 ppm O 460 ppm Ca



(a) (b)

Fig. 3 Scanning electron micrographs of Ti_3Al powders reduced by CaH_2 for 43.2 ks at 1223 K (a) and 1323 K (b), respectively. CaO was removed by leaching. The oxygen contents of these powders were analyzed to be 4500 and 2600 ppm for (a) and (b), respectively.

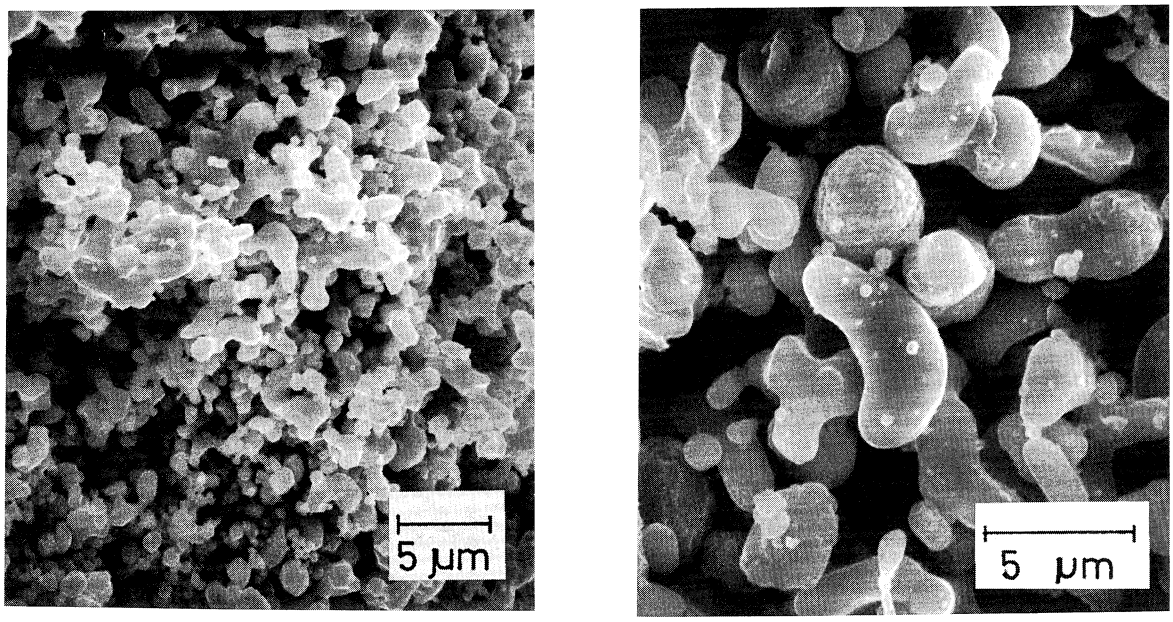


(a) (b) (c)

Fig. 4 Scanning electron micrographs of Ti_3Al powders reduced by CaH_2 at 1273 K for 10.8 ks (a), for 43.2 ks (b) and for 86.4 ks (c). CaO was removed by leaching. The oxygen contents of these powders were analyzed to be 2600, 2100 and 2100 ppm for (a), (b) and (c), respectively.

at 1273 K for 3.6–180 ks. According to the phase diagram[11], Ti–Al alloys in a lower aluminum concentration than 8.6 mol%Al should have the high temperature form, β-Ti, at 1273 K, but the obtained powders in this compositional range were still hexagonal even when the vessel containing the reduced sample was rapidly cooled into water were from the reduction temperature. They must have, therefore, transformed into α-Ti during cooling. The lattice constants of the hexagonal α-Ti and Ti_3Al phases obtained by this co-reduction technique using CaH_2 were plotted in Fig. 6 against the nominal aluminum composition of the starting oxide mixture. For comparison, the compositional ranges of the stable phases at 1273 K are in the upper part of Fig. 6, which is cited from the latest Ti–Al phase diagram[11]. The lattice constants coincided well with the previous measurements made on the bulk samples[14]-[17], and with our previous report of the co-reduction experiments by vapor calcium[7]. The measured lattice parameters decrease smoothly in each phase, showing that the powders obtained by this method have the same aluminum concentration as the bulk alloys.

Figure 7 shows the relationship between the nominal and analytical aluminum contents of the reduced powders. The nominal compositions were fairly well maintained also in the final alloys although the data were somewhat scattered in the region of aluminum content more than 40 mol%Al, where Ti_3Al and TiAl coexist.



(a) (b)

Fig. 5 Scanning electron micrographs of Ti_3Al powders reduced at 1273 K for 10.8 ks by calcium vapor (a) and calcium liquid (b). CaO was removed by leaching.

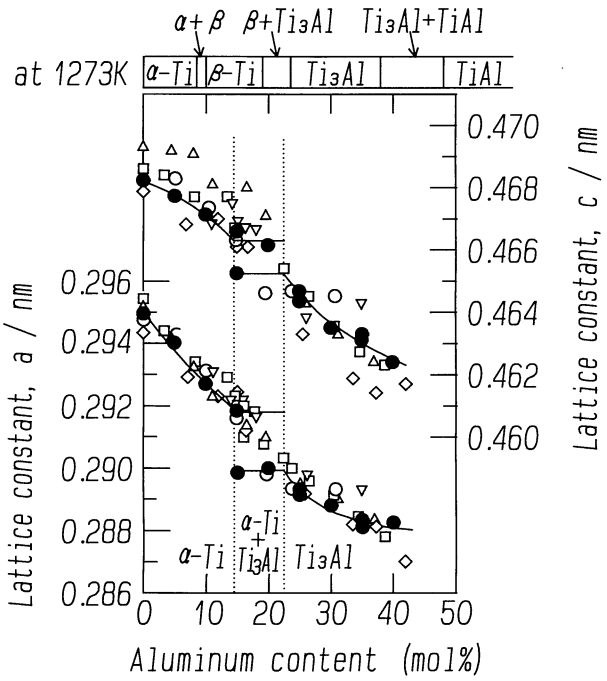


Fig. 6 Lattice constants of the hexagonal phases after reduction by CaH_2 at 1273 K for 43.2 ks. The symbols in the figure are as follows; ●: This study by CaH_2, ○: Suzuki *et al.* by calcium vapor[7], △: Ogden *et al.*[14], ◇: Bumps *et al.*[15], □: Clark *et al.*[16] and ▽: Crossley[17].

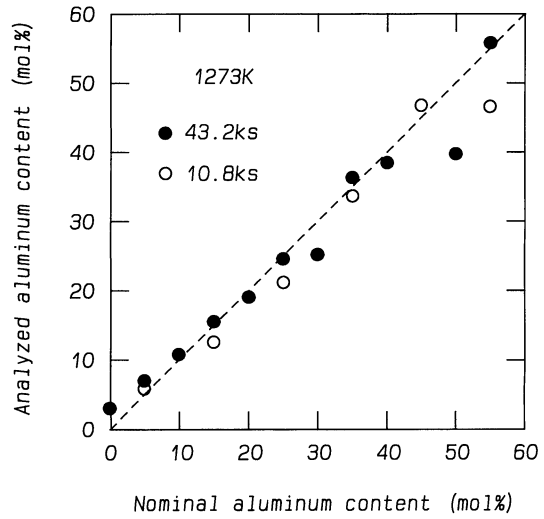


Fig. 7 Analyzed aluminum contents against the nominal aluminum compositions in the starting oxide mixture. The nominal compositions are shown as the ratio of Al/(Al+Ti). The open and closed circles show the analyzed values of the specimens reduced at 1273 K for 10.8 ks and 43.2 ks.

3. Preparation of TiAl

By using CaH_2 as the reducing agent, TiAl single phase was successfully produced after the reduction at 1273 K from either the calcined oxide mixture or the mechanically mixed oxides, which contained Ti and Al with the atomic ratio of 1:1. Ti–50 mol%Al powder formed by this procedure was about 1 μm in particle size and contained about 3000 ppm oxygen and 1150 ppm calcium on the average of six independent runs.

For the reduction of the oxide mixture containing Ti and Al with the ratio of 1:1, however, Ti_3Al compound and $CaAl_2$ were preferentially produced in addition to TiAl, both when the excessive amount of vapor calcium or liquid calcium was used and when the reduction time was longer than 10 ks at 1273 K. The same result has already been reported elsewhere[7]. For the powder reduced by using 1.2 to 2.0 times the stoichiometric amount of CaH_2, only TiAl was detected by the X-ray diffraction.

However 3.0 times the stoichiometric amount produced the mixture of TiAl and Ti_3Al after the reduction and leaching. The evidence of the loss of aluminum atoms for the reduced powders were also shown in Fig. 7. The formation of Ti_3Al coexisting with TiAl depended on the quantities of CaH_2, as mentioned above.

IV. Discussion

1. Oxygen content in the reduced compound

Oxygen contents have been experimentally achieved to be about 2000 mass ppm for pure titanium[12] and 800–2400 ppm for Ti-6Al-4V alloy[18] by the calciothermic method using liquid calcium, although the lowest limit of oxygen content in titanium wire at 1273 K is 500 ppm[19] or 650 ppm[20], which has been achieved only from thermodynamic equilibrium among titanium, calcium, and calcium oxide. Because of the lack of information about the solubility limit of oxygen in Ti_3Al and TiAl, and about their thermodynamic data for oxygen, it cannot be judged at this stage whether our oxygen content attained experimentally (1200 ppm at lowest) is reasonable. Figures 3 and 4 show that the oxygen content in the reduced Ti_3Al powders depends on the particle size. This means that the oxygen content is considerably affected by the re-oxidation on the surface of the fine particles occurring during handling in air after the reduction.

2. Calcium hydride as a reductant

CaH_2 has been considered to decompose completely into calcium and hydrogen gas below 1273 K[21][22]. Based on these data, CaH_2 may attack the oxide mixture as a form of vapor calcium or liquid calcium at the reduction temperature. CaH_2 powder could be blended with oxides better than calcium granules and located more closely near the oxide mixtures. Therefore, CaH_2 powder can have wider reaction area with the oxide mixture than calcium granules, and CaH_2 might be able to decrease the oxygen content in Ti_3Al more effectively than the vapor or liquid calcium.

The thermodynamic data[13][23]–[25], however, show that CaH_2 does not decompose completely and a part of CaH_2 remains in its solid or liquid form even in the reduction temperature range if the decomposed hydrogen gas does not escape from the vessel: the equilibrium hydrogen pressure at its melting temperature, 1273 K[23], has been evaluated to be 29[23], 48[24] or 63 kPa[13][25]. Residual CaH_2 can contribute directly to the reduction of the oxides, and hydrogen gas is produced by the reaction.

Since the initial reductant, CaH_2, could not be found after the reduction, the former mechanism might be possible. However, due to no other supporting evidences we cannot judge which mechanism operated. No matter which mechanism takes place in the case when CaH_2 is used, however, hydrogen gas is produced during the reduction and it gives higher pressure to the reduction vessel: if the charged CaH_2 decomposed completely, for example, the hydrogen pressure would arrive to a few tens of MPa. Most of the hydrogen gas might leak out of the vessel from the gap between the vessel and the lid, or diffuse through the stainless steel wall, but this is not a serious problem for the reduction of oxides, because hydrogen gas can thermodynamically reduce TiO_2 only to Ti_2O_3[23]. In this paper, the stoichiometric amount of CaH_2 was calculated by assuming hydrogen gas reduces no oxide.

3. Ti–Al–Ca–O phase diagram

Figures 8 and 9 show the evaluated phase equilibria in the Ti–Al–Ca–O quaternary system at 1273 K, which were calculated by the binary phase diagrams[9]–[11][26]–[31] and a reasonable extrapolation of the thermodynamic data[13][23][25][31]–[35], supposing that there is no complex oxide containing three metallic selements and no compound in the Ti–Al–Ca ternary system. We also neglected the solubilities of oxygen in TiO[26][30][31] and in liquid calcium[27], and the existence of higher Magneli phases[26] in the Ti–O system because their data were unknown or unreliable, but they do not significantly affect the results in Fig. 8. From Fig. 8, it is obvious that there are no Ti-containing oxides at the oxygen partial pressure below $\log (P_{O_2}/\mathrm{Pa}) = -29.58$, and no Al-containing oxides below $\log (P_{O_2}/\mathrm{Pa}) = -31.00$. No oxides except for CaO can stably exist at the oxygen partial pressure of Ca–CaO ($\log (P_{O_2}/\mathrm{Pa}) = -36.37$). Even if some complex oxides exist stably in the Ti–Al–Ca–O system, for example, $CaTi_3Al_8O_{19}$[36], and even if some transient phases such as TiO and Ti_2O_3 are formed on the way of the reduction, they can be decomposed to a metallic state in the successive reduction.

The activities of aluminum at 1273 K in the Ti–Al and Ca–Al systems were evaluated by the regular solution approximation using the reported thermodynamic values[23][33]–[35]. The activities in both systems showed large negative deviations from the ideal solution. Based on the calculated activities and the reported thermodynamic data[23], the phase equilibria and the conjugation lines were estimated on the Ti–Al–Ca ternary diagram in Fig. 9, taking account of the experimental results in this work that the solubilities of calcium in Ti_3Al and TiAl were very small. However, since there was no report about the solubilities of calcium in $TiAl_3$ nor of titanium in $CaAl_2$, they are neglected in Fig. 9.

The phase equilibria in Fig. 9 show that α-Ti and β-Ti are in equilibrium with almost pure liquid calcium, i.e. at maximum 0.55 mol%Al and 1.59 mol%Al, respectively. But the region coexisting with Ti_3Al and TiAl is in equilibrium with the liquid Ca–12.2 mol%Al alloy, and TiAl single phase can coexist with the calcium liquid for a wide compositional range between 12.2 and 48.4 mol%Al at 1273 K. Metallic titanium and Ti_3Al after the reduction are, therefore, equilibrated with calcium rich Ca–Al alloys, but the TiAl phase cannot be equilibrated with this Ca-dilute aluminum alloys. This is due to the fact that since an excessive amount of calcium is used for the reduction of these experiments because of leakage of calcium vapor, the obtained TiAl powders lose

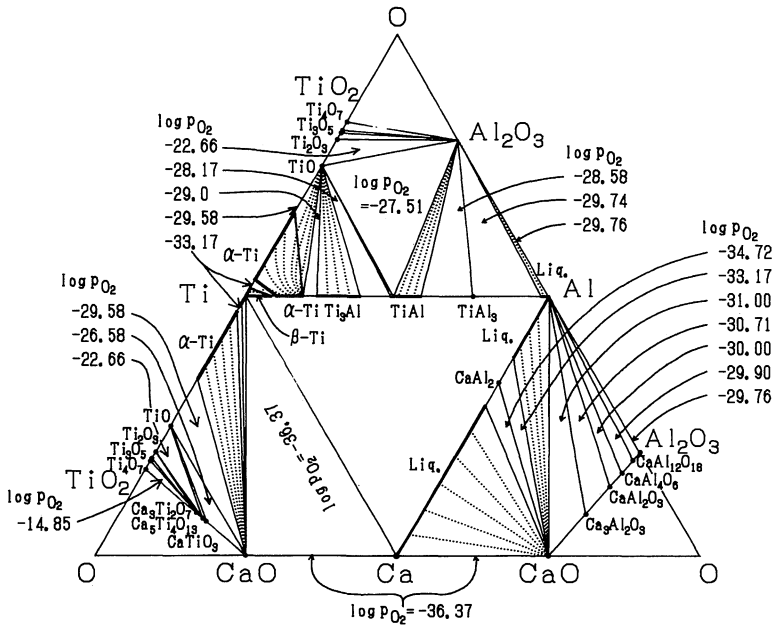


Fig. 8 Calculated phase diagrams of three ternary systems of four elements at 1273 K. The phase equilibria were estimated by the oxygen partial pressure and binary phase diagrams[9)-(11)(13)(25)-(35)] of four elements. The figure also shows the logarithm of the oxygen partial pressure (log (P_{O_2}/Pa)) in the ternary systems.

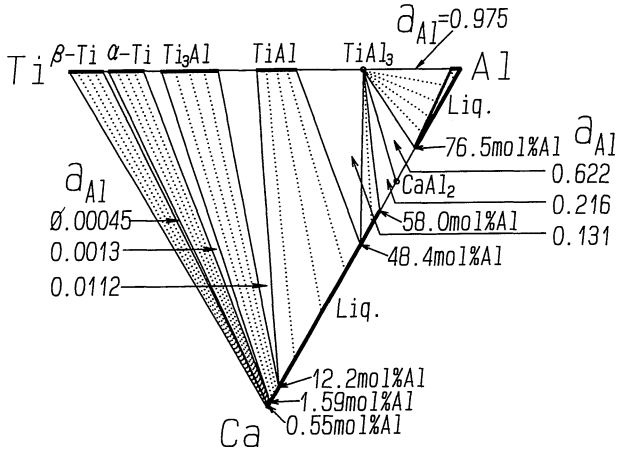


Fig. 9 Calculated phase diagram and aluminum activity (a_{Al}) of the Ti-Al-Ca ternary system at 1273 K.

aluminum after their reduction by producing Ca-Al alloys. This may be the reason why some analyzed aluminum contents over 40 mol%Al were slightly lower than the nominal content as shown in Fig. 7. In producing the TiAl phase by using liquid or vapor calcium, Ti_3Al and $CaAl_2$ were detected after the co-reduction. According to the phase equilibria mentioned above, $CaAl_2$ may be formed during solidification of aluminum rich calcium liquid alloy. When quite an excessive amount of CaH_2 was used for the preparation of TiAl, Ti_3Al was also detected in addition to TiAl. This suggests that neither CaH_2 nor hydrogen gas significantly change the phase equilibria shown in Fig. 9 even if hydrogen lowers the activity of calcium when CaH_2 coexists with calcium[24]. TiAl might coexist, therefore, with Ti_3Al and aluminum rich Ca-Al liquid when the amount of CaH_2 is excessive for the reduction. For further quantitative discussion, information about the Ti-Al-Ca-O-H system is required.

V. Conclusion

The clean and fine Ti_3Al and TiAl compound powders were produced directly from the oxide mixtures of TiO_2 and Al_2O_3 by calciothermic reduction using vapor calcium, liquid calcium or CaH_2. This procedure consists of three steps: raw oxide blending, co-reduction and leaching. The methods for the preparation of the oxides mixtures had no effect on the production of the powders of a desired composition. The use of CaH_2 powder for the reduction gave better results than that of the other reductants on oxygen contents in the reduced powders. The lowest impurities in the Ti_3Al powder were 1200 mass ppm oxygen and 180 ppm calcium.

The thermodynamic considerations for the preparation of stoichiometric TiAl single phase in this calciothermic process were base on the construction of Ti-Al-Ca ternary phase diagrams.

Acknowledgments

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