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Instructions for use

Preparation of Ti-V-Cr Hydrogen Absorption Alloy Powder

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Abstract: A new method was developed to synthesize the hydrogen storage alloy powders directly from the oxide mixtures. Calcium co-reduction and the molten $CaCl_2$ was applied to reduce the oxides and to form the target alloy simultaneously. As the fundamental confirmation, the binary Ti-V solid solution and the intermetallic compound $TiCr_2$ were prepared. Their oxygen content was controlled below 0.5mass% and the compositional variation of metallic elements was within 5mol% from the desired compositions. These alloy powders could absorb hydrogen after the normal activation treatment.

Keywords: Hydrogen Storage, Material Synthesis, Molten Salt Chemistry, Reduction of Oxide, Intermetallic Compound.

1. INTRODUCTION

Metallic vanadium (V) is one of a few elements that can absorb hydrogen even at room temperature and near at an ambient pressure [1]. Many attempts focused on alloying in V in order to reduce the amount of precious V because of its poor abundance, to suppress the surface contamination and to enhance hydrogen absorption and evolution. Ti-V-Cr alloy is nominated at present as one of the interesting candidates [2-6].

One of the practical problems of V based alloys is its high cost. The cost reduction in preparation of the hydrogen storage alloys is one of key issues for practical application, because the conventional procedure needs many heat cycles from the raw materials, *i.e.*, oxide ores, as shown in Fig. 1(a).

A new process is studied to synthesize the hydrogen storage alloy directly from its oxide mixture, as shown in Fig. 1(b). The binary alloy consisting of 30 mol%Ti-70 mol%V and the intermetallic compound of $TiCr_2$ were chosen as the examples, aiming at the ternary Ti-V-Cr alloy in future. The purpose of this work is to confirm the proposed process in the fundamental binary systems. These binary products are also known as hydrogen storage alloys [7-9].

Fig. 1 Preparation methods of hydrogen storage alloy powder.

2. PROPOSED METHOD

Here we propose a method using the co-reduction technique [10-16] that the oxide mixture is simultaneously reduced to the powder of a hydrogen storage alloy. Titanium oxide (TiO_2, 40 mass% oxygen) has the strongest affinity with oxygen among the related oxides. When calcium is applied as the reductant, even TiO_2 can be reduced in a single step to a metallic state. For example, the oxygen level in Ti is only 500 mass ppm oxygen when in equilibrium [17,18], and 2000 ppm experimentally [19,20]. The reaction temperature is enough

low such as at 1073-1273 K. The co-reduction using calcium was reported as a successful method to synthesize Ti-Al and Nb-Al alloys [10-14] or intermetallic compounds such as $SmCo_5$ and Nb_3Sn [15,16].

However, the by-product CaO precipitates on the surface of the formed metallic powder and it disturbs the successive reduction, deoxidation and alloying, as shown in Fig. 2. The *in situ* elimination of CaO by dissolution into the molten $CaCl_2$ was successful in Ti powder formation from TiO_2 and Nb_2O_5 [21,22], and in deoxidation of Ti [18,23]. This is because about 20 mol%CaO can dissolve in the molten $CaCl_2$ [24-26]. A few mol%Ca can dissolve also in it [27-29] and react effectively with the oxides. $CaCl_2$ is thermodynamically stable in this strong reducing atmosphere, and the excess amounts of Ca and $CaCl_2$ after the reaction are easily soluble in water and environmentally friendly.

Based on these properties, Fig. 1(b) illustrates our proposal to synthesis the ternary alloy powder for hydrogen storage [30,31].
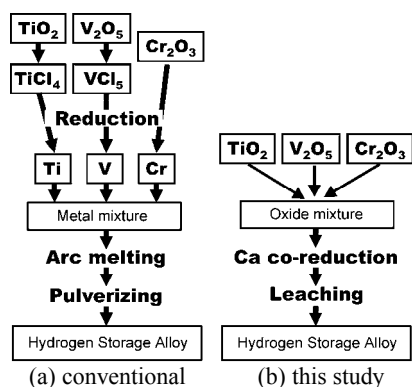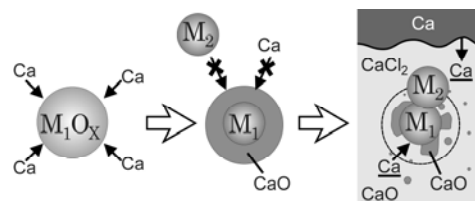

Fig. 2 Mechanism of CaO formation and elimination.

3. PREPARATION OF Ti-V BINARY ALLOY

3.1 Reduction using V_2O_5

The most stable oxides powder, V_2O_5 and TiO_2, (both <1μm in particle size) were mixed mechanically in the mortar, and reduced by liquid Ca in the sealed stainless vessel. When $CaCl_2$ was not used, a large amount of Ca was evaporated by a significant exothermic reaction, and a heterogeneous product was obtained in which $CaTiO_3$ and some complex oxides in the Ca-V-O ternary system were coexisted. When $CaCl_2$ was used, the co-reduction effectively progressed after the optimizations of the charging method, the molar fractions of Ca, $CaCl_2$ and oxide mixture, and the reaction conditions such as temperature and time. A large amount of metallic powder was successfully recovered by leaching.

The most stable oxide, V_2O_5, melts at 954 K [32]. Note that

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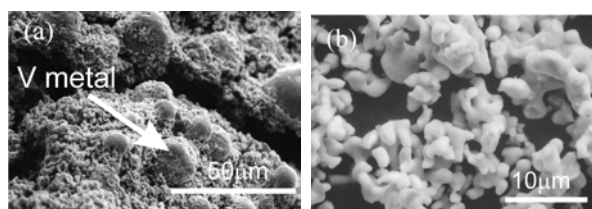
Fig. 3 Images by scanning electron microscopy (SEM) of co-reduced powders. Powder (a) and (b) were started from the oxide mixtures using V_2O_5 and V_2O_3, respectively.

Ca reduction occurs effectively above melting point of Ca (1112 K [32]). Therefore, V_2O_5 is reduced from its liquid state (for example, at 1173 K). V_2O_5 is preferentially reduced to V metal prior to reduction of TiO_2, because the oxygen potentials of vanadium oxides are thermodynamically higher than that of TiO_2 [32,33]. The droplets of V sometimes covered spherically on the surface of TiO_2 as shown in Fig. 3(a). $CaTiO_3$ and Ti_3O were detected by X-ray diffraction (XRD) with Ti-V BCC phase in a short reaction time, and these titanium oxides were reduced to α-Ti in a prolonged time. However, this Ti particles formed with delay did not combine completely with V, probably because of the morphology of V precipitation and of isolation by molten $CaCl_2$.

The oxygen concentration in this powder was analyzed to be 1.18 mass%O, which was higher than the reported value (0.142 mass%O) in the Ti powder reduced from pure TiO_2 in $CaCl_2$ by Ca [21]. This high oxygen content reflects the facts that the V metal reduced preferentially covered the oxide mixture, especially TiO_2, and that the deoxidation from the BCC solid solution was delayed. Fig. 4 illustrates the sequence of co-reduction starting from the oxide mixture of V_2O_5 and TiO_2.
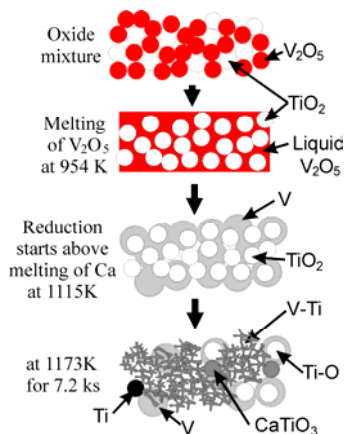
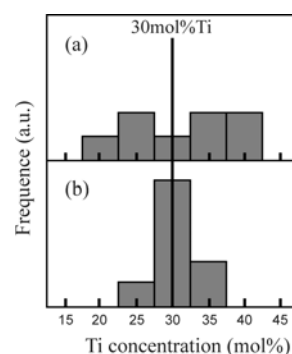**Fig. 4** Illustration of heterogeneous co-reduction mechanism when V_2O_5 is used as one of starting oxides.

3.2 Reduction using V_2O_3

Instead of low melting V_2O_5, V_2O_3 with the same particle size was applied, because its melting point is 2340 K [32]. Note that V_2O_3 can be obtained by the weak reduction of V_2O_5, for example, in the hydrogen gas flow. The reduction of V_2O_3 by Ca is less exothermic than that of V_2O_5 [32].

When the oxide mixture of V_2O_3 and TiO_2 was reduced by Ca in the molten $CaCl_2$, a single phase of BCC structure was obtained as judged by XRD patterns, when the sample were reacted at 1173 K for 72 ks in the molten $CaCl_2$. The oxygen concentration was as low as 0.5 mass%. The obtained powder looked like a coral and it has a wide surface area (See Fig.3(b)) that seems to be suitable for quick hydrogen

absorption and evolution. Energy dispersive X-ray (EDX) analysis showed the homogeneous metallic concentration over all the particles. The metallic concentration profiles for many grains were analyzed as shown in Fig.5(b), where the target concentration was 30 mol%Ti. A slight coarsening of the reduced particles is needed to obtain the homogeneous metallic content. It is noteworthy that this homogeneity was better than that by the conventional arc melting, where the dendritic crystal growth occurs during cooling.

Fig. 6 illustrates the reaction sequence and morphology change when the oxide mixture containing V_2O_3 was used.

Fig. 5 Concentration distributions in the obtained Ti-V powders. (a) starting from V_2O_5 and TiO_2, and (b) starting from V_2O_3 and TiO_2.
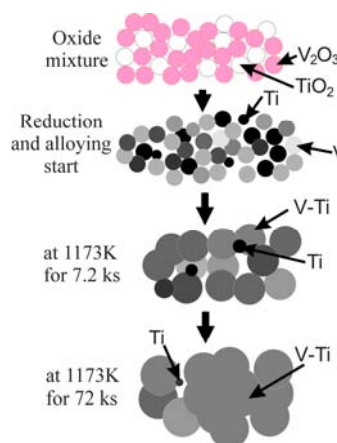

Fig. 6 Illustration of homogeneous co-reduction mechanism when V_2O_3 is used as one of starting oxides.

3.3 Hydrogen storage capacity

The hydrogen storage curves were measured at 313 K for powders obtained from a mixture of V_2O_5 and TiO_2, and from that of V_2O_3 and TiO_2. The dissolution of the excessive Ca, CaO and $CaCl_2$ in the aqueous solution was accompanied by an exothermic reaction, hydrogen gas evolution and increase at the pH of the solution. Although a small amount of hydrogen might be absorbed in this leaching process, the initial hydrogen in the powder was neglected in the analysis. Assuming that the powders consisted of the BCC single phase of 30mol%-70mol%V, the absorbed hydrogen (H/M) was evaluated as shown in Fig. 7.

When the powders were freshly exposed to the purified hydrogen gas atmosphere of 3.5 MPa at 313 K, the hydrogen absorption remains at a very low level. An activation treatment was needed prior to the measurements of the hydrogen storage curves, which was taken as a standard procedure for hydrogen absorption. It is because an oxide or
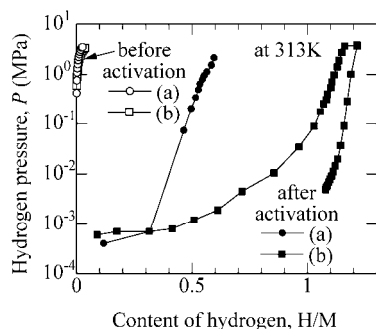
Fig. 7 Pressure-composition isotherms for the samples (a) from the oxide mixture of V_2O_5 and TiO_2 and (b) from that of V_2O_3 and TiO_2.

organic layer generally contaminates the sample surface. The surface of the powder might be contaminated during the handling. Therefore, the samples were activated by three cycles of evacuation at 723K and hydridation at 313K [7-9]. The rate of hydrogen absorption was slow at 313 K even after the activation. As shown in Fig. 7, the pressure increment at H/M=1.0 reflects the hydride formation. The total amount of the charged hydrogen was larger in the sample produced from V_2O_3 than in that produced from V_2O_5. Its larger hydrogen absorption capacity is due to the compositional homogeneity. Because some differences in the isotherm of these samples were observed compared to the arc-melted V-20mol%Ti alloy [2,3,7], we may need a more precise study, considering the optimized activation process and measuring conditions.

4. PREPARATION OF TiCr₂

The V-Ti alloy shows the complete solubility, however, the solubility of the intermetallic compound $TiCr_2$ is only 2mol% [33], and it was difficult to synthesis the homogeneous $TiCr_2$ by conventional arc melting. The long heat treatments were needed for compositional homogenization. This study attempted to prepare $TiCr_2$ by the proposed route in Fig. 1 from the mixture of TiO_2 and Cr_2O_3. Note that Cr_2O_3 is only one stable oxide in the Cr-O binary system.

The in-situ dissolution of CaO in the molten $CaCl_2$ was required to reduce the oxide mixture effectively, as found in Ti-V binary system. In all the other experiments, $CaCl_2$ was charged to enhance the co-reduction and leaching.

The powder obtained at 1173 K was fine powder of α-$TiCr_2$. The oxygen content decreased to a level of 0.3-0.6 mass%O in a short time as shown in Fig. 8, and the residual or intermitting oxides were not detected by XRD as shown in Fig. 9. According to the equilibrium phase diagram of Ti-Cr binary
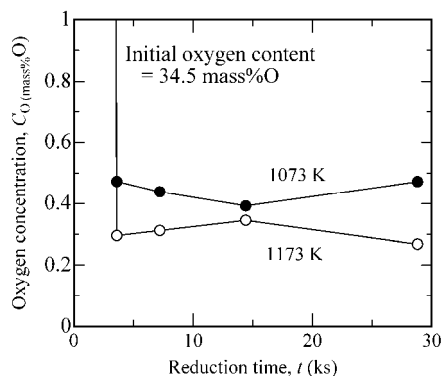

Fig. 8 Oxygen content in the obtained α-$TiCr_2$ powder.
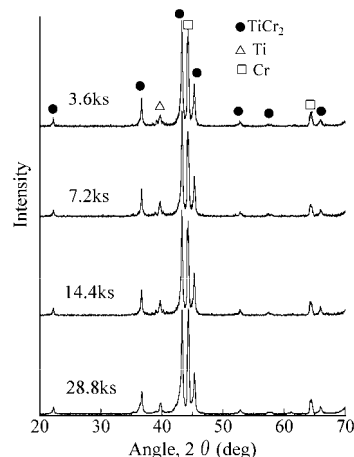
Fig. 9 XRD patterns for $TiCr_2$ samples reduced at 1173 K.

system [33], two phases of high temperature form α-$TiCr_2$ and low temperature form β-$TiCr_2$ coexists at our reaction temperatures, 1073 and 1173 K. β-$TiCr_2$ in our samples could be transformed to α-$TiCr_2$ during cooling. A faint amount of α-Ti and Cr remained even after the long reaction time or by a small adjustment of starting composition (Fig.9). This is because the stable concentration range of α-$TiCr_2$ is very narrow [33]. Fig.10 shows the sequence of phase formation in the Ti-Cr binary system. It is important to mix the starting oxide powder more precisely in a microscopic level, however, the precipitation during cooling can not be avoided because of slow cooling in the solidified salt.
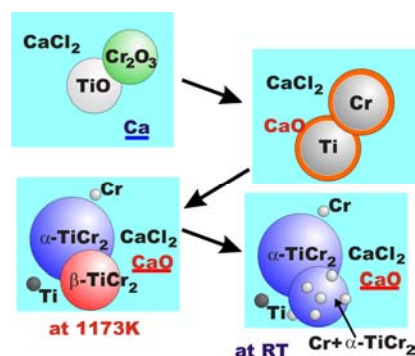

Fig. 10 Illustration of homogeneous co-reduction mechanism when V_2O_3 is used as one of starting oxides.

Hydrogen absorption property of the reduced samples was measured after the normal activation treatment as shown in Fig.11. This PCT curve was similar with that of the α-$TiCr_2$ sample that was arc melted and annealed for a long time below 1073 K [1,34]. The arc-melted sample without annealing contained β-$TiCr_2$, and its hydrogen absorption property was affected by the coexistence of β-$TiCr_2$. (Note that both α-$TiCr_2$ and β-$TiCr_2$ can absorb hydrogen.) The reduced samples did not show such behavior due to two phase-mixture. Although the reduced sample contained a small amount of Ti and Cr, its hydrogen absorption was operated only by α-$TiCr_2$ phase.

4. CONCLUSIONS

We proposed a new method consisting of calcium co-reduction and *in situ* separation of CaO. The oxide mixture
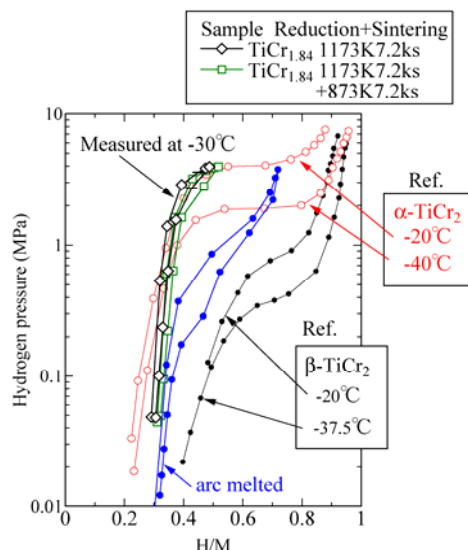
Fig. 11 Pressure-composition isotherms for the samples from the oxide mixture of Cr_2O_3 and TiO_2 in molar ratio of $TiCr_{1.84}$. The plateau in [34] could not be measured because of limitation of apparatus (the lowest temperature and the highest pressure).

is reduced by metallic Ca to form a Ti-V alloy or α-$TiCr_2$ powder directly. The by-product CaO is removed into the molten $CaCl_2$ simultaneously. The usage of $CaCl_2$ for synthesis was efficient for CaO elimination, and hindered the formation of intermediate phases such as $CaTiO_3$.

Because V_2O_5 melts at a lower temperature than the temperatures where the reaction occurs, and because V_2O_5 was reduced preferentially, metallic V covered the TiO_2 particles and the reduction became heterogeneous. The existence of V film hindered the successive reduction of TiO_2 and the formation of a homogeneous alloy. When the refractive V_2O_3 was mixed with TiO_2 as the starting mixture, a single BCC phase was successfully obtained when Ca and $CaCl_2$ were used. The deviation of the Ti concentration was within 5 mol%Ti, and the oxygen content decreased to 0.5 mass%. The activated powder showed capability of hydrogen absorption.

For synthesis of $TiCr_2$, this proposal was also effective when the reduction was conducted in the molten $CaCl_2$. A fine α-$TiCr_2$ powder was acceptably deoxidized to a level of 0.5%O, although a faint amount of Ti and Cr remained. This powder showed the similar hydrogen absorption capacity with that of the reported α-$TiCr_2$.

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