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<tr>
<td>Citation</td>
<td>Proceedings of the JGSEE and Kyoto University Joint International Conference on Sustainable Energy and Environment (SEE). Hua-Hin, Thailand, December 1-3, 2004, 167-170</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2004</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/50115">http://hdl.handle.net/2115/50115</a></td>
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<tr>
<td>Type</td>
<td>proceedings</td>
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<tr>
<td>File Information</td>
<td>SEE2004_167-170.pdf</td>
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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 CaCl₂ 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 TiCr₂ were prepared. Their oxygen content was controlled below 0.5 mass% and the compositional variation of metallic elements was within 5 mol% 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 TiCr₂ 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].

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 (TiO₂) melts at 954 K [32]. Note that the most stable oxide powder, V₂O₅ and TiO₂ (both <1 µm in particle size) were mixed mechanically in the mortar, and reduced by liquid Ca in the sealed stainless vessel. When CaCl₂ was used, a large amount of Ca was evaporated by a significant exothermic reaction, and a heterogeneous product was obtained in which CaTiO₃ and some complex oxides in the Ca-V-O ternary system were coexisted. When CaCl₂ was used, the co-reduction effectively progressed after the optimizations of the charging method, the molar fractions of Ca, CaCl₂ 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, V₂O₅ melts at 954 K [32].
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_3 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.

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. 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.

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
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\textsubscript{2}O\textsubscript{3} than that produced from V\textsubscript{2}O\textsubscript{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 TiCr\textsubscript{2}

The V-Ti alloy shows the complete solubility, however, the solubility of the intermetallic compound TiCr\textsubscript{2} is only 2mol% [33], and it was difficult to synthesis the homogeneous TiCr\textsubscript{2} by conventional arc melting. The long heat treatments were needed for compositional homogenization. This study attempted to prepare TiCr\textsubscript{2} by the proposed route in Fig. 1 from the mixture of TiO\textsubscript{2} and Cr\textsubscript{2}O\textsubscript{3}. Note that Cr\textsubscript{2}O\textsubscript{3} is only one stable oxide in the Cr-O binary system. The in-situ dissolution of CaO in the molten CaCl\textsubscript{2} was required to reduce the oxide mixture effectively, as found in Ti-V binary system. In all the other experiments, CaCl\textsubscript{2} was charged to enhance the co-reduction and leaching.

The powder obtained at 1173 K was fine powder of \(\alpha\)-TiCr\textsubscript{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 system [33], two phases of high temperature form \(\alpha\)-TiCr\textsubscript{2} and low temperature form \(\beta\)-TiCr\textsubscript{2} coexists at our reaction temperatures, 1073 and 1173 K. \(\beta\)-TiCr\textsubscript{2} in our samples could be transformed to \(\alpha\)-TiCr\textsubscript{2} during cooling. A faint amount of \(\alpha\)-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 \(\alpha\)-TiCr\textsubscript{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.

4. CONCLUSIONS

We proposed a new method consisting of calcium co-reduction and in situ separation of CaO. The oxide mixture
is reduced by metallic Ca to form a Ti-V alloy or α-TiCr2 powder directly. The by-product CaO is removed into the molten CaCl2 simultaneously. The usage of CaCl2 for synthesis was efficient for CaO elimination, and hindered the formation of intermediate phases such as CaTiO3. Because V2O3 melts at a lower temperature than the temperatures where the reaction occurs, and because V2O5 was reduced preferentially, metallic V covered the TiO2 particles and the reduction became heterogeneous. The existence of V film hindered the successive reduction of TiO2 and the formation of a homogeneous alloy. When the refractive V2O3 powder was mixed with TiO2 as the starting mixture, a single BCC phase was successfully obtained when Ca and CaCl2 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 TiCr2, this proposal was also effective for CaO elimination, and hindered the formation of intermediate phases such as CaTiO3.

Fig. 11 Pressure-composition isotherms for the samples from the oxide mixture of Cr2O3 and TiO2 in molar ratio of TiCr1.54. The plateau in [34] could not be measured because of limitation of apparatus (the lowest temperature and the highest pressure).

ACKNOWLEDGMENTS

The authors thank Mr. K. Tatemoto and H. Kitagawa at Kyoto Univ., Dr. H. Takenishi at Kansai Univ. and Prof. Dr. J. Sestak at Czech Academy of Science for their useful suggestions. They thank Mr. Unesaki for his experimental assistance of SEM observation and EDX analysis. This work was financially supported in part by the Kyoto Univ. 21st Century Core of Excellence (21COE) Program and by the Grants-in-Aid for Scientific Research under Contract No. 14205109.

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