Preparation of Hydrogen Storage Ti-V-Cr Alloy from the Oxide Mixture in CaCl₂

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The mixture of TiO₂, V₂O₃ and Cr₂O₃ powders were reduced simultaneously inside the basket-type of cathode in the molten CaCl₂, where the by-product CaO was returned to the reductant Ca by the electrolysis. A fine metallic particles consisting of the BCC solid solution and a small amount of Ti₃Cr₂ phase were successfully obtained after 10.8 ks at 1173 K. The oxygen concentration was in the level of 2000 mass ppm. The carbon contamination due to CO₂ gas evolution at the anode during the electrolysis could be avoided by the electrode arrangement in the melt. The compositional homogeneity in the sample was improved by the rapid cooling, because the BCC solid solution decomposes during the slow cooling from 1173 K. This sample could absorb about 1.9 mass % hydrogen at maximum, and the effective (reversible) hydrogen storage was 1.68 mass %, which approached to 87.5% of the previous reports.

Keyword: oxide mixture, electrolysis, calciothermic reduction, molten salt, calcium chloride, hydrogen storage alloy

1. Introduction

V-Ti-Cr based solid solution with body-centered cubic (BCC) structure has been developed to be one of the promising hydrogen storage alloys1. In the industrial production of the elemental metals in this alloy, the Ti oxide is once converted to the chlorides and reduced by Mg, and Cr and V are extracted by the electrolysis or reduction by Al or Si. For alloying, these elemental metals are arc-melted several times, heated for homogenization, and pulverized. As shown in Figure 1(a), this long process wastes thermal and chemical energy. It may become a barrier for mass production of this alloy.

This work proposes a simplified synthesizing process to save energy consumption. Figure 1(b), illustrates our proposal that the oxide mixture is simultaneously reduced and converted to the alloy powder2. The co-reduction using calcium was reported as a successful method to synthesize Ti-Al, Nb-Al and Ti-V binary alloys or intermetallic compounds such as SmCo₅, Nb₃Sn and TiCr₂2,3. The purpose of this work is to apply the co-reduction technique to the formation of hydrogen storage alloys with the combination of CaO electrolysis in the molten CaCl₂.

2. Concepts

Ti has a stronger affinity with oxygen than V and Cr, as evaluated from the oxygen potential of the binary systems4 of Ti-O, V-O and Cr-O in Figure 2. Oxygen in equilibrium with metallic Ti is also shown5. The Ca/CaO equilibrium can decrease the oxygen content in Ti to 0.05 mass% level. Namely, Ca can reduce all the V, Ti and Cr oxides to their metals with a low oxygen level. When Ca is reacted with the oxide mixture, we can expect alloying with these metals, i.e., reaching a lowest state of energy, in addition to the reduction. Previous attempts of Ca co-reduction, however, showed higher residual oxygen content than inferred from the thermodynamic evaluation and the alloys were relatively heterogeneous3. This is because the by-product CaO of this reduction disturbs the reduction and alloying, as illustrated in Figure 3(b). Okabe et al. proved in the deoxidation of pure Ti that a lower oxygen content than that in the Ti/Ca/CaO equilibrium was attainable when molten CaCl₂ was applied6, because CaCl₂ could dissolve, for example, about 20 mol% CaO at 1173 K7. The dissolution of the by-product CaO in-situ into the molten CaCl₂ was successfully applied to enhance the Ca reduction of TiO₂8.
Disturbance of CaO for alloying (a)(b) and CaO dissolution into the CaCl₂ melt during co-reduction by Ca dissolved in CaCl₂ (c).

Proposal for alloy powder in CaCl₂ combined with OS process. For the alloy synthesis, we expect that the reduction, the deoxidation and the alloying would be accelerated by the addition of CaCl₂, as shown in Figure 3(c). The alloying between the metallic M₁ and M₂ will be enhanced by the CaO removal into the molten CaCl₂, although Ca liquid flows above the molten CaCl₂. It is noted that Ca can dissolve for a few mol% in the CaCl₂, and that CaCl₂ and its mixed salts can work as a strong reducing atmosphere. Additionally we plan to recycle the by-product CaO to the reductant Ca using the concept of CaO electrolysis in the molten salt, known as "OS process".

Figure 4 illustrates the final concept to synthesis the ternary Ti-V-Cr alloy powder directly from the oxide mixture. Ca electrochemically precipitates at the cathode from the dissolved CaO, and it dissolves near the cathode as the reductant for the oxide mixture that is injected near the cathode. The oxygen ion is removed as CO or CO₂ gas by reacting with the carbon anode as,

$$\text{Ca}^{2+} (\text{in CaCl}_2) + 2e^- = \text{Ca} (\text{in CaCl}_2)$$ (1)
$$2 \text{O}^{2-} (\text{in CaCl}_2) + \text{C} = \text{CO}/\text{CO}_2 (\text{gas}) + 2 \text{e}^-$$ (2)
$$\text{MO + Ca(in CaCl}_2) = \text{M} + \text{Ca}^{2+} + \text{O}^{2-}$$ (3)
$$\text{M}_1 + \text{M}_2 + \text{M}_3 = (\text{M}_1\cdot\text{M}_2\cdot\text{M}_3 \text{ alloy})$$ (4)

For example, the theoretical decomposition voltages necessary for CaO and CaCl₂ are 2.6 and 3.21 V, respectively, at 1173 K⁴. Those for CO₂ and CO gas evolution are lowered to 1.63 and 1.54V, respectively, if the carbon anode is used as eq.(2). The voltage increase due to the activity changes of Ca and CaO is evaluated < 0.1 V¹⁰.

In case of this proposal, we may control the reduction rate using the supplied current, while the calciothermic reduction can not be well controlled because of its significant exothermic heat³,⁸.

3. Experimental

This work used oxide powders with high purity (>99%) and sub micron size, TiO₂ (rutile type), Cr₂O₃ and V₂O₅. They were well mixed in the mortar at the atomic ratio of 20mol%Ti-30%Cr-50%V. Granular CaCl₂ anhydrate (about 3500 g, 99.0%) and 0.5mol% CaO were used after heating in vacuum above 873 K. As shown in Figure 5, the carbon crucible (120mm ID., 320mm in height) was used as anode, and the Ti net (#100) was used as the holder (15mm ID, 60mm in height) of oxide powder (3g) and simultaneously as the cathode. They were heated at 1173 K in a purified Ar gas atmosphere. After the electrolysis at 1173 K, the sample in the cathode was cooled and rinsed with the distilled water to remove the solidified salt. Subsequently it was washed in acetic acid, water and ethanol for several times, centrifugally separated, and dried in vacuum.

The phases in the recovered samples were identified by X-ray diffraction (XRD) measurement using Cu-Kα radiation. The oxygen and hydrogen concentrations were analyzed by an inert gas fusion — infrared absorption method using LECO TC500C and RH402, respectively. The powder morphology was examined by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray analyzer (EDX). The hydrogen storage property was measured by the Sievelts method at 293 K.

4. Results and Discussion

During the electrolysis the gas bubbling at the anode was clearly observed after 1.2 ks, and the black or gray powders...
were obtained after 10.8-86.4 ks when 2.5-3.0V was applied. The average current density at the cathode and anode were 220-320 and about 10 mA/cm², respectively. The recovered powders were mainly the BCC solid solution with a small amount of TiCr₂ by XRD phase identification, as shown in Figure 6(a). The oxygen contents were in the level of 2000-4400 mass ppm. This means that the co-reduction worked well when the sufficient amount of electric charge was applied. When a smaller amount of CaCl₂ (2.0 kg) was used, the oxygen level was as high as 4.92%. Some lower oxides and TiC contaminated the sample. This is because a fairly large portion of CO/CO₂ gas that evolved from the bottom of carbon crucible reacted with Ca that was generated in the molten salt. Because the distance ratio of two electrodes, S/B, was 1.83 in this setup (See Figure 5), the gas bubbles happen to enter the reducing zone near the cathode, and they were reduced to C. When S/B=0.55 and the bottom surface was covered by an Al₂O₃ plate, the sample was well reduced and no carbon contamination was found. This shows that the flow of gas bubbles should be isolated from the cathodic area to give a strong reducing capacity for Ca.

When the samples were cooled in the molten salt or in the furnace, a small amount of TiCr₂ was found by XRD analysis. TiCr₂ phase can coexist with the BCC solid solution at the higher temperatures and at the wide compositional region, as shown in Figure 711). Note that both the BCC and TiCr₂ phases can absorb hydrogen, but the former was considered superior11).

Although the phase diagram was not known below 973 K, TiCr₂ phase might precipitate during our slow cooling from 1173 K with the solidified salt. Some samples were rapidly cooled by pulling up the cathode to the upper part of the furnace and by blowing the cool Ar gas. Figure 6(b), shows that the precipitation of TiCr₂ phase was hardly found in these samples. Figures 8. and 9. show the SEM images and their elemental mappings in these samples. The primary particles in the obtained powder are a few μm in size, and they are slightly sintered and look like the coral with a wide surface area, suitable for hydrogen absorption. The segregation due to TiCr₂ precipitation is found in Figure 7, while the elemental distribution is more homogeneous in the rapidly cooled sample (Figure 8).

The intensity ratio of XRD diffraction peaks assigned for the BCC structure and the TiCr₂ phases are used for a quantification of volumic ratio of the precipitated TiCr₂ phase, as shown in Figure 10. The cooling rate was monitored by the thermocouple attached with the cathode surface. Figure 11. shows the PCT curve at 293K of the rapidly cooled sample. Our sample absorbed about 1.9 mass% hydrogen at maximum after the normal activation procedure11). The effective hydrogen storage is evaluated as 1.68mass%H, which is about 87.5% of the reported value at 298K for the arc-melted and well-annealed sample11).
5. Conclusion

This work confirmed a proposal that the calciothermic co-reduction of the oxide mixture can form a fine alloy powder directly, and that the by-product CaO in the reduction can be recycled to the reductant Ca by the molten salt electrolysis, so called as "OS process". This new proposal will be applicable as the general production process for the alloy powder.

Acknowledgements

This work was supported in part by 21st COE program at Kyoto University, Taiyo Kokou Co. Ltd., and a Grand-in-Aid from the Japanese Ministry of Education, Science, Culture and Sports, #14205109 and #18360367.

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