

**Preparation of Hydrogen Storage Alloys
from the Oxides
by Calcium Co-reduction in Molten CaCl₂**

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The cost reduction of the hydrogen storage alloys is one of keys for practical application. As shown in Fig.1, the conventional procedure needs many heat cycles from the raw materials, i.e., oxide ores. A new process is studied to synthesize the hydrogen storage alloy directly from its oxide mixture. This method is operated in the molten CaCl₂ and it combines the calcium co-reduction and the *in situ* dissolution of the by-product CaO, as shown in Fig.2. Because of a strong reducibility of Ca, the stable oxide of TiO₂ can be reduced to Ti with only 500 ppm oxygen in a step. The dissolution of CaO is useful to enhance the reduction, deoxidation and alloying. The residual Ca and CaCl₂ are easily soluble in water and environmentally friendly.

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 well-homogenized Ti-V solid solution and □-TiCr₂ were obtained from the mechanical mixture of refractive V₂O₅ and TiO₂, and of Cr₂O₃ and TiO₂, respectively. The molten CaCl₂ was indispensable in both cases to complete the reaction.

The melt of V₂O₅ covered the residual TiO₂ and it was preferentially reduced to V particles, as shown in Fig.3(a), which prohibited the subsequent reduction and alloying. However, the usage of refractive V₂O₃ could promote the co-reduction, decrease the oxygen content and produce a good quality of powder with the homogeneous concentration. Morphology of the obtained powders was commonly coral-like slightly sintered fine particles, as shown in Fig.3(b). Their wide surface area seems suitable for the hydrogen absorption.

The narrow stoichiometric compound TiCr₂ could be also formed in the molten CaCl₂. A tiny amount of Ti and Cr coexisted with the low-temperature phase, □-TiCr₂, although the reaction temperature and time were varied. These alloy powders showed the hydrogen storage capacity after the normal activation treatment, as shown in Fig.4.

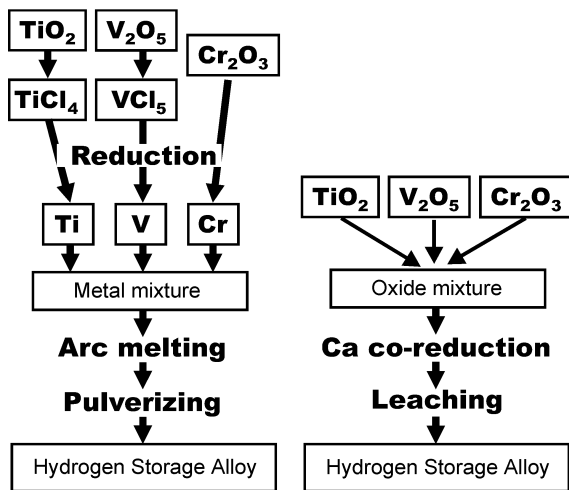


Fig.1 Conventional and developed processes.

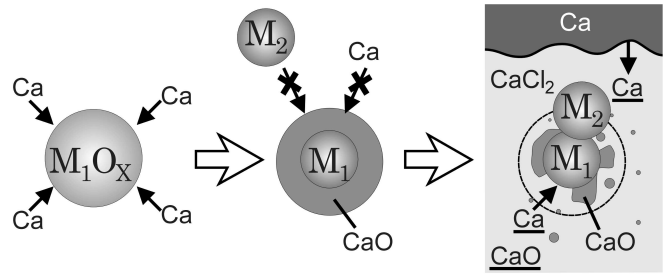


Fig.2 Mechanism of Ca reduction, alloying and dissolution of CaO into the molten CaCl₂.

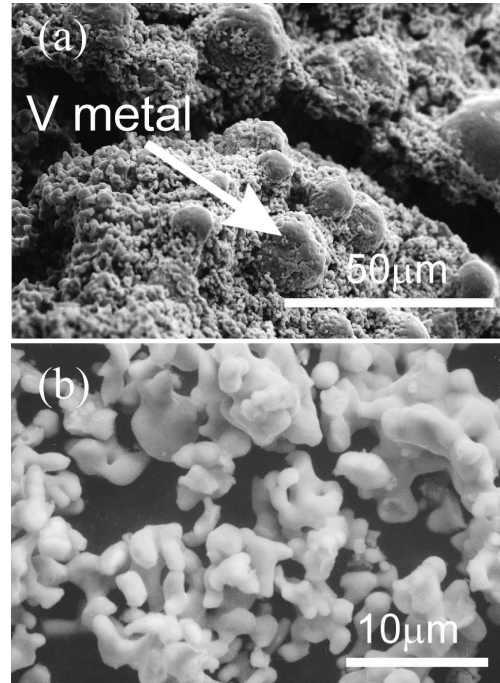


Fig.3 SEM images of the powder obtained (a) from TiO₂+V₂O₅ and (b) from TiO₂+V₂O₃.

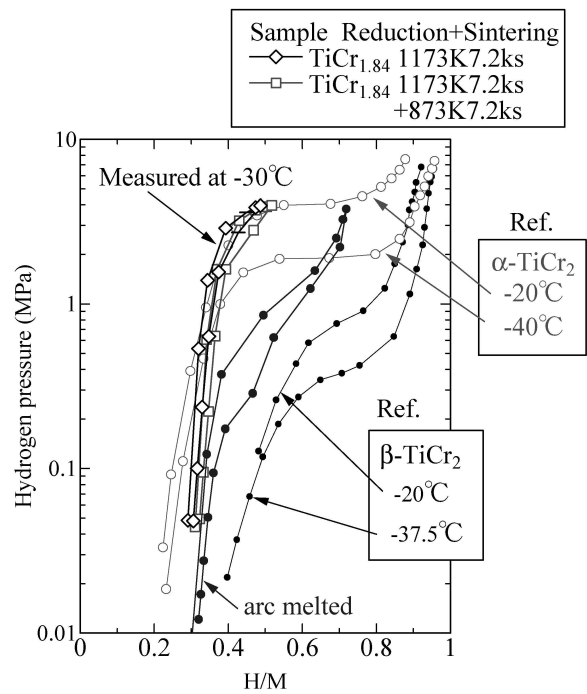


Fig.4 PCT diagram of the reduced TiCr₂ powder.