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Hydrogen absorption properties of Ti_3Al-based ternary alloys

K. Ishikawa[a,*], K. Hashi[a], K. Suzuki[b], K. Aoki[a]

[a]*Department of Materials Science, Kitami Institute of Technology, Koen-cho 165, Kitami, Hokkaido 090-8507, Japan*
[b]*School of Physics, The University of New South Wales, Sydney 2052, Australia*

Abstract

The structure, the hydrogen capacity and the hydrogen desorption behavior of hydrogenated Ti_3Al-based alloys substituted with Nb, Mo, Pd, Ta and W were investigated by XRD and a hydrogen analysis with the aim of selecting effective elements to improve the hydrogen absorption–desorption properties of a binary Ti_3Al alloy. The relation between the hydrogen capacity and the 50% hydrogen desorption temperature was plotted in the diagram obtained in the previous work. Mn, Co, Ni and Nb were selected to be effective elements to reduce the hydrogen desorption temperature, although they gave rise to reduction in the hydrogen capacity.

Keywords: Hydrogen absorption; TDS (thermal desorption spectrum); Ti_3Al; Amorphous; bcc phase

1. Introduction

The $D0_{19}$-Ti_3Al is a particularly attractive candidate for new hydrogen absorption materials because of its large hydrogen capacity and low density. Although this alloy absorbs more than 3 wt.% hydrogen [1,2], the hydrogen desorption temperature is too high for practical applications [2].

We have reported the hydrogen absorption–desorption properties of the binary and ternary Ti_3Al-based alloys [3]. In the case of stoichiometric Ti_3Al, the crystal structure changes from $D0_{19}$ to fcc type (CaF_2) by hydrogenation. The amount of hydrogen absorbed in this alloy is 1.45 H/M, i.e. 3.32 wt.%. Resulting from our investigations of ternary Ti_3Al alloys substituted with V, Cr, Mn, Fe, Co, Ni, Cu, Zr and Hf, it is found that hydrogen absorption–desorption properties depend on the crystal structure of their hydrides. The amorphous hydrides, formed in the alloys substituted with Zr or Hf, showed a large amount of hydrogen capacity, but desorbed it at a higher temperature than that of binary Ti_3Al hydride. The bcc hydrides, obtained by the addition of V or Cr to Ti_3Al, showed a little hydrogen capacity. On the contrary, the substitutional elements such as Mn, Co and Ni, which form the C14 Laves type hydride in ternary Ti_3Al-based alloys, have an ability to reduce the desorption temperature without prominent decrease of the hydrogen capacity.

In this study, the effects of the elements of Nb, Mo, Pd, Ta and W on the hydrogen absorption–desorption properties of Ti_3Al-based ternary alloys are investigated with the aim of selecting useful elements to improve the hydrogen absorption–desorption properties of binary Ti_3Al.

2. Experimental

The alloys expressed as $Ti_{75-x}Al_{25}M_x$ (M=Nb, Mo, Pd, Ta and W, x=0, 15 and 25 at.%) were prepared by arc melting under an Ar atmosphere. The ingots were pulverized and then sieved through 50-mesh screen. An activation treatment was carried out at 673 K for 3.6 ks in vacuum of 1.0×10^{-3} Pa. Then powder samples were reacted with ultra high purity hydrogen (7N) of 5 MPa at room temperature for 173 ks. The crystal structure of the samples before and after hydrogenation was identified with an X-ray diffractometer (XRD) using Cu Kα radiation monochromated by graphite. The amount of hydrogen absorbed in the samples and thermal desorption spectrum (TDS) were examined by a hydrogen analyzer with a heating rate of 2 K/s.

3. Results and discussion

Fig. 1 shows the TDS of $Ti_{60}Al_{25}Nb_{15}$ hydride heated with 2 K/s. The broken line represents the hydrogen signal

*Corresponding author.
E-mail address: ishikazu@king.cc.kitami-it.ac.jp (K. Ishikawa).

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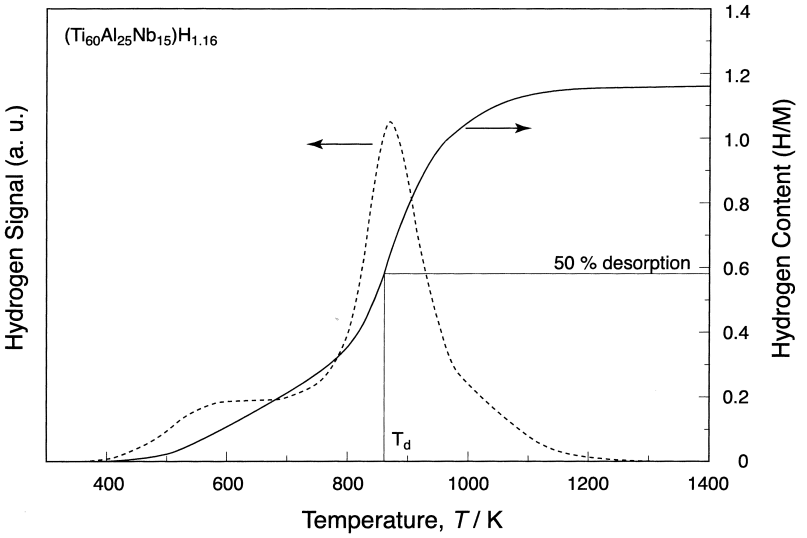

Fig. 1. TDS of $Ti_{60}Al_{25}Nb_{15}$ hydride heated at a rate of 2 K/s. The broken and the solid line correspond to the desorption rate and the amount of desorbed hydrogen, respectively. The temperature at which half of the absorbed hydrogen was desorbed is for convenience defined as the 50% hydrogen desorption temperature (T_d) in this study.

upon hydrogen desorption, which corresponds to the desorption rate of hydrogen at the temperature. Two peaks overlapping each other are observed in the TDS. The temperature of the peak is considered to be related to the energy state of the hydrogen occupation site [4]. Therefore, hydrogen atoms may occupy two different sites in this hydride. On the other hand, the solid line obtained by the integration of the absorption rate shows the amount of hydrogen desorbed from the sample. The number and the shape of the peaks vary with the kind and the amount of the ternary elements. Therefore, the temperature at which half of the absorbed hydrogen was desorbed is defined as the 50% hydrogen desorption temperature (T_d) for the comparison. The T_d of the $Ti_{60}Al_{25}Nb_{15}$ hydride is about 860 K.

The amount of hydrogen absorbed in the Ti_3Al-based ternary alloys is plotted against the concentration of the element M in Fig. 2. The hydrogen content of the ternary Ti_3Al-based hydrides decreases monotonously with increasing the amount of the element. The degree of the reducing hydrogen capacity is relatively small in the alloys substituted with Nb or Ta. For instance, the alloy substituted with 25 at.% Nb absorbs about 1.0 H/M. On the other hand, the amount of hydrogen absorbed in the alloys substituted with Pd, Mo or W decreases rapidly with alloying.

Fig. 3 shows T_d as a function of the amount of element M. To understand the change of T_d, structures of the alloys before and after hydrogenation (in parentheses) are denoted in this figure. The T_d changes in a complex manner in contrast to the hydrogen capacity. The T_d of the hydrides alloyed with Mo or W is reduced by 15 at.% addition, but rises by 25 at.% addition, i.e. T_d shows a minimum at 15 at.% of Mo and W. The XRD data indicate that these hydrides substituted with 15 at.% Mo and W consist of a mixture of bcc and unidentified crystalline phases (X). On the other hand, the hydrides substituted with 25 at.% Mo or W have a bcc single phase structure or bcc+bcc two-phase structure, respectively. The XRD analysis shows that these two bcc phases are considered to

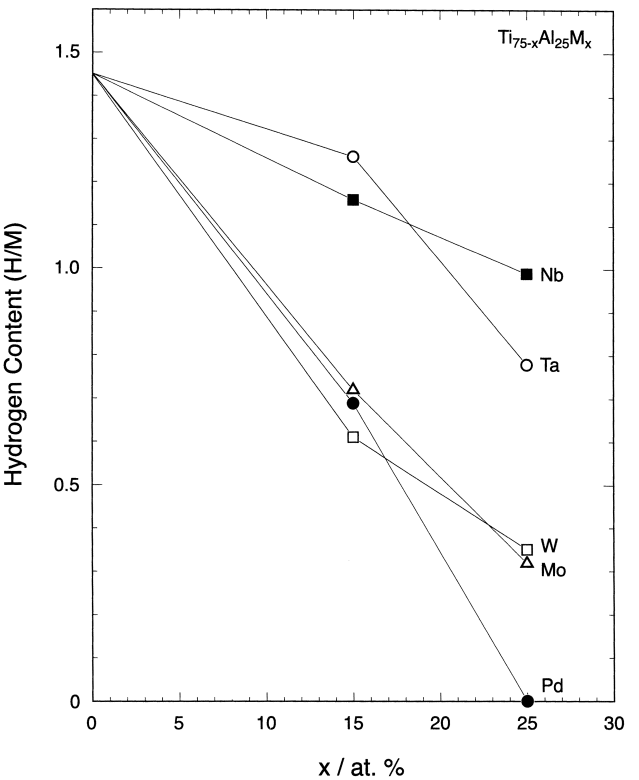

Fig. 2. The amount of hydrogen absorbed in $Ti_{75-x}Al_{25}M_x$ alloys against the atomic content of substituted element M.

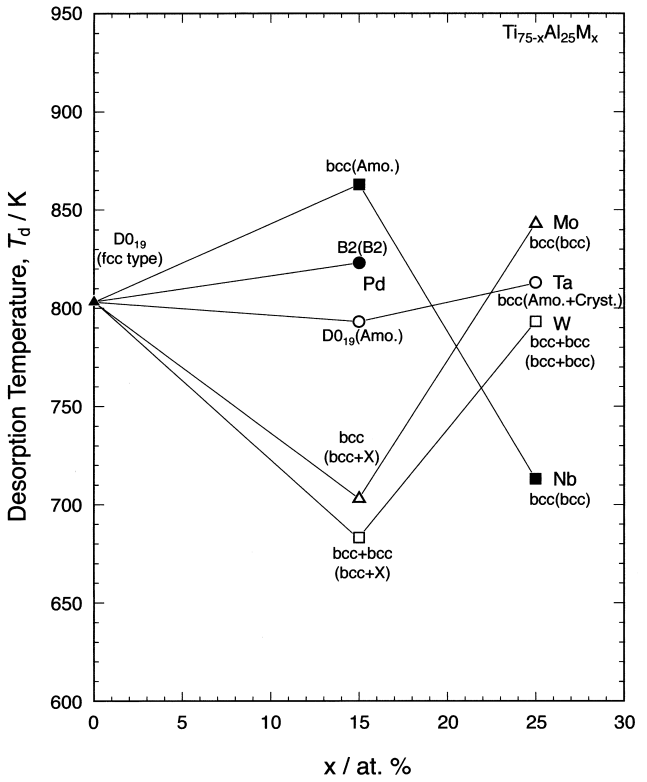

Fig. 3. Desorption temperature T_d of ternary alloys as a function of alloying content. The structure of the alloys before and after hydrogenation (in parentheses) are denoted in this figure.

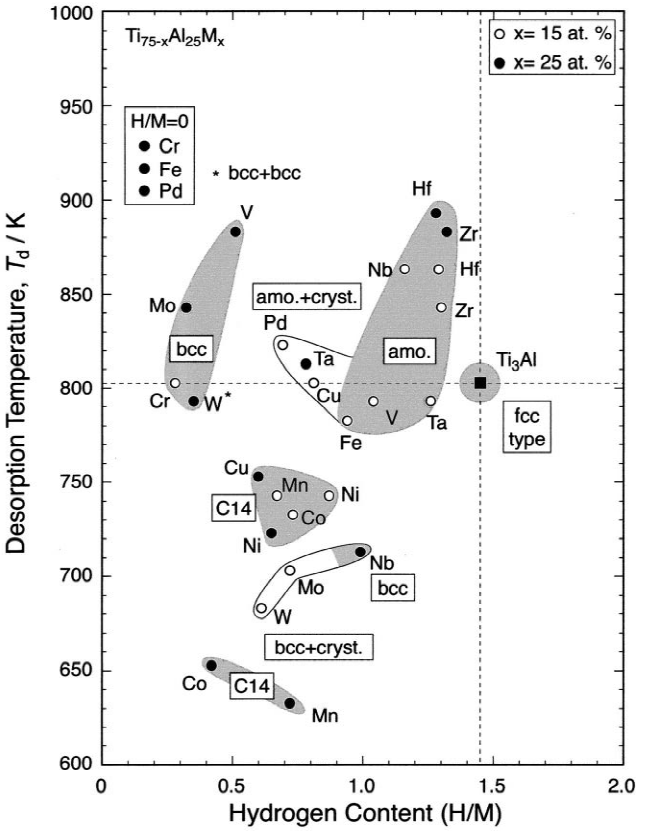

Fig. 4. The relation between the amount of hydrogen absorbed in the alloys and desorption temperature T_d along with our experimental data reported in Ref. [3]. The data points which correspond to the same crystal structure of hydrogenated state are located in separate gray areas.

be β-Ti and W solid solution. The difference of the crystal structure of the hydrides between 15 and 25 at.% addition affects T_d. It is worth noticing that the X phase reduces the desorption temperature. Although the presence of the X phase is effective for reducing T_d, its detail is still uncertain at the present stage. In the case of the alloy substituted with 15 at.% Nb, T_d rises at once, but reduces by 25 at.% addition, i.e. T_d shows a maximum at 15 at.% of Nb. The original alloys substituted with 15 and 25 at.% Nb have a bcc structure, but their hydride of 15 or 25 at.% Nb addition shows an amorphous or a bcc structure, respectively. In our previous work [3], hydrogen-induced amorphization has been confirmed in the alloys substituted with V, Fe, Zr and Hf under the same experimental condition, and these hydrides tend to have high T_d. Therefore, the amorphous hydrides are generally stable rather than the crystalline hydrides. The amorphous phase may raise the T_d of the alloy substituted with 15 at.% Nb. The T_d in the alloys substituted with 25 at.% Nb or 15 at.% Mo or W is around about 700 K, which is about 100 K lower than that of binary Ti_3Al hydride. Therefore, Nb, Mo and W are concluded to be effective to reduce the hydrogen desorption temperature.

The relation between the hydrogen capacity and the 50% hydrogen desorption temperature (T_d) is plotted in the diagram obtained in the previous work [3] in Fig. 4. The crystal structures of these hydrides are mainly classified into four groups, i.e. fcc type, amorphous, bcc and C14 Laves type hydrides. The data with the same crystal structure are located in separate gray areas. We can see a clear relation between the hydrogen absorption–desorption properties and the crystal structure of hydrides.

Firstly, the hydrogen capacity and the desorption temperature of ternary hydrides are compared with those of binary Ti_3Al in order to select the useful elements to improve the hydrogen absorption–desorption properties. We can notice that the hydrogen capacity is reduced regardless of what kind of elements are substituted with binary Ti_3Al. Next, the effect of each substitutional element on the hydrogen desorption temperature is discussed. Assuming the border line at $T_d = 770$ K, the elements located above the line, which are V, Cr, Fe, Zr, Pd, Hf and Ta, 15 at.% Cu and Nb and 25 at.% Mo and W, have no effect on reducing the hydrogen desorption temperature. Therefore, we conclude that these elements are useless under the present experimental conditions. The alloy hydrides substituted with these elements form an amorphous or a bcc phase. On the contrary, the desorption temperature in the alloys substituted with the elements located below the border line, i.e. Mn, Co and Ni, 15 at.% Mo and W and 25 at.% Cu and Nb, are reduced. Therefore,

these elements are effective to reduce the hydrogen desorption temperature. The alloys substituted with these elements form a C14 Laves or a bcc hydride. Especially, the alloys substituted with 25 at.% Mn or Nb show a large reduction of desorption temperature with minimum decrease of hydrogen capacity under present experimental conditions, so that a further possibility may be expected.

4. Summary and conclusions

In the present and previous work, the hydrogen absorption–desorption properties of Ti_3Al-based ternary alloys were investigated by XRD and a hydrogen analysis. The crystal structure of ternary hydride, which classified into amorphous and bcc, affects strongly the hydrogen absorption–desorption properties. The hydrogen capacity of binary Ti_3Al hydride is reduced by the addition of whatever substitutional element. However, the alloys substituted with Mn, Co and Ni, 15 at.% Mo and W and 25 at.% Cu and Nb show a reduction of hydrogen desorption temperature. Especially, the alloy hydrides with 25 at.% Mn or Nb show a large reduction of desorption temperature with minimum decrease of hydrogen capacity.

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