Emergence of Hydrogen Absorption Ability in Metastable HCP, FCC and Amorphous Ti–Al Alloys Prepared by Mechanical Grinding

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Titanium aluminides [L1 0 -TiAl (Ti 0 50Al 0 50 and Ti 0 40Al 0 60), TiAl 2 and D0 22 -TiAl 3 ] have been mechanically ground (MG) in an argon atmosphere. In addition, hydrogen absorption and desorption properties of the MG-alloys have been investigated. Hcp- and amorphous (α-) TiAl, fcc- and α-TiAl, and fcc-TiAl 2 are formed by mechanical grinding (MG) of TiAl, TiAl 2 and TiAl 3 , respectively. Although original Ti–aluminides do not absorb hydrogen, hcp- and α-TiAl, and fcc- and α-TiAl 2 , prepared by MG, having a fresh surface absorb hydrogen of the amount of 0.4 – 0.1 (H/M). The present work clearly demonstrates that MG is a useful technique for an emergence of the hydrogen absorption ability of intermetallic compounds containing much hydride-forming elements.

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1. Introduction

In recent years, new hydrogen storage materials with a lightweight and a large hydrogen capacity have been strongly desired. Generally, hydrogen storage alloys are made by a combination of a hydride forming and a non-forming element. Since the Ti–Al system consists of a hydride-forming element (Ti) and a non-forming element (Al), and both of them are lightweight elements, Ti-aluminides are expected to form by nonequilibrium processes such as mechanical grinding (MG). It is interesting whether these metastable Ti–Al alloys prepared by MG absorb hydrogen or not. In this paper, we report on structural and morphological changes of Ti–Al compounds by MG in an argon atmosphere. Furthermore, we report on hydrogen absorption and desorption properties of MG–Ti–Al alloys. The present paper clearly demonstrates that both hcp- and α-TiAl (where α stands for amorphous), fcc- and α-TiAl 2 with a fresh surface can absorb hydrogen of the amount of 0.4 – 0.1 (H/M).

2. Experimental

L1 0 -TiAl (γ phase, Ti 0 50Al 0 50 and Ti 0 40Al 0 60), TiAl 2 (Ti 0 33Al 0 67) and D0 22 -TiAl 3 (Ti 0 25Al 0 75) intermetallic compounds were prepared by arc melting of titanium (99.8%) and aluminum (99.999%) in a purified argon atmosphere. These ingots were pre-pulverized by a hand mill. The alloy powder was put into a stainless steel container (SUS304) together with stainless steel balls (SUS304, 3/8-inch diameter). The weight ratio of ball-to-powder was 20/1. The container and the lid were sealed with an O-ring. The container was evacuated to 2 × 10 – 2 Pa for 7.2 ks with a diffusion pump and then filled with argon gas (99.9999%) at 0.2 MPa. MG experiments were carried out for selected times using a planetary type-high energy ball mill (ITOH, LA-PO.4) with a rotation speed of 2.5 rps. After evacuation of argon gas, MG–Ti–Al powders were reacted with high purity 5 MPa hydrogen (99.99999%) at room temperature for 86 ks. Structures of alloyed Ti–Al powders after MG and of hydrogenated ones were identified by X-ray diffractometry (XRD) using Cu Kα radiation. Size and morphology of MG–Ti–Al alloys were observed by scanning electron microscopy (SEM). The thermal stability of MG–Ti–Al alloys was examined using a differential scanning calorimeter (DSC) at a heating rate of 0.67 K/s in an argon flowing atmosphere. The hydrogen absorption capacity (C H ) and a thermal desorption spectrum (TDS) of hydrogen were measured by a hydrogen analyzer (HORIBA, EMGA-621) at a heating rate of 2 K/s. The temperature where the half of absorbed hydrogen was desorbed is defined as the 50% hydrogen desorption temperature, T d .

3. Results

(a) TiAl

Figure 1 shows XRD patterns of stoichiometric alloyed TiAl (Ti 0 50Al 0 50) powder mechanically ground for selected times in 0.2 MPa argon gas. The original TiAl (MG 0 ks) takes an L1 0 structure. After MG for 22 ks, the Bragg peaks of L1 0 –TiAl are weakened and broadened by strain induced by MG. After MG for 86 ks, the Bragg peaks of the L1 0 structure are disappeared and, in place of them, new Bragg peaks of the hcp phase are observed. Although the intensity ratio of main Bragg peaks for this phase is same as that of D0 22 –TiAl, no superlattice line is observed. Then, we call this phase as hcp-TiAl. The Bragg peaks for hcp-TiAl are replaced with a broad peak after MG for 720 ks. The DSC curve of this sample shows an exothermic peak of crystallization as will be shown later. Consequently, TiAl mechanically ground for 720 ks is concluded to be amorphous and denoted as amorp-
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Fig. 1 XRD patterns of TiAl powder mechanically ground for selected times in 0.2 MPa argon.

The Fe contamination introduced from stainless steel balls and the vessel was checked by inductively coupled plasma (ICP) atomic emission spectrometry. The Fe content in the samples was 1.1 and 2.0 mass% for 173 and 720 ks MG, respectively. This amount of Fe contamination may be negligible for the structural evolution and the hydrogen absorption capacity.

Figures 2(a)–(c) show SEM photographs of hcp- and α-TiAl alloys prepared by MG. An as-pulverized sample (MG 0 ks) shows a cleavage fracture mode and the particle size is larger than 200 μm. After MG for 86 ks (hcp-TiAl), particles are rounded and their size is reduced to about 30–50 μm. The particle size is reduced by further milling and the particles become spherical with a size of about 30–40 μm after 720 ks (α-TiAl).

Figure 3(a) shows DSC curves of hcp- and α-TiAl powders prepared by MG. Hcp-TiAl shows a broad exothermic peak around 850 K, while α-TiAl does two exothermic peaks around 880 K and 1000 K.

Figure 3(b) shows XRD patterns of hcp-TiAl heated to the points (i–iii) in the DSC curve. Since the Bragg peaks of the samples heated to (i) and (ii) are indexed on the basis of the hcp and the L1₀ structures, respectively, the exothermic peak around 850 K results from the transformation from the hcp into the L1₀ phase.

Figure 3(c) shows XRD patterns of α-TiAl heated to the points (iv–vi) in the DSC curve. The samples heated up to the points (iv), (v) and (vi) have the amorphous, the hcp-type and the L1₀ structure, respectively. Here, the position of the Bragg peaks for the sample heated to the point (v) is same as those of the hcp-TiAl, but the intensity ratio of them is different with those of it. Then, we call this phase as hcp-type TiAl. The sample of α-TiAl crystallizes into hcp-type TiAl at the first step and then transforms into the L1₀-TiAl. Hcp-TiAl prepared by MG is stable up to about 800 K, but hcp-type TiAl transformed from α-TiAl is stable up to 920 K. This difference in the thermal stability may result from the different amounts of lattice defects. Both hcp- and α-TiAl phases heated to 1070 K show small amount of Bragg peaks due to impurity phases. These impurity phases may be introduced by the Fe contamination. The enthalpy change for the...
Exothermic

\[ 50 \text{ J/mol K} \]

\[ a\text{-TiAl} \]

\[ \text{hcp-TiAl} \]

\[ 600 \quad 700 \quad 800 \quad 900 \quad 1000 \quad 1100 \]

\[ T \text{ / K} \]

(a) TiAl, DSC in Ar

Fig. 3 (a) DSC curves of hcp-TiAl and \( a\)-TiAl, and XRD patterns of (b) hcp-TiAl and (c) \( a\)-TiAl heated to the respective stages (i–vi) in DSC. An unknown phase is marked with \( x \).

Figure 3 shows DSC curves of hcp-TiAl and \( a\)-TiAl, and XRD patterns of hcp-TiAl and \( a\)-TiAl. The transformation from hcp- into L1\(_{0}\)-TiAl is \(-3.3\) kJ/mol. The enthalpy change for crystallization from \( a\)-TiAl into hcp-type TiAl, and for the transformation from the hcp-type TiAl into L1\(_{0}\)-TiAl are evaluated to be \(-4.6\) and \(-3.9\) kJ/mol, respectively. On the other hand, the CHALHAD calculation gives an enthalpy difference of about 4.0 kJ/mol between hcp-TiAl and L1\(_{0}\)-TiAl. The experimentally determined enthalpy change for the hcp-L1\(_{0}\) transformation is almost in agreement with the expected value.

Figure 4 shows XRD patterns of original L1\(_{0}\)-TiAl, and hcp-TiAl and \( a\)-TiAl prepared by MG before and after hydrogenation. These samples were reacted with 5 MPa H\(_2\) at room temperature for 86 ks without exposure to air. No shift of the Bragg peaks for L1\(_{0}\)-TiAl and of the broad peak for the amorphous alloy is observed. On the contrary, the Bragg peaks of hcp-TiAl shift slightly to the lower angle side, indicating that hcp-TiAl absorbs hydrogen keeping its original crystal structure.

Figure 5 shows thermal desorption spectrum (TDS (solid line)) of hydrogen, and the amount of absorbed hydrogen (dash-dotted line) for both hcp-TiAl and \( a\)-TiAl. TDS expresses the hydrogen desorption rate at the temperature, and by integration of TDS the amount of desorbed hydrogen is measured. On heating the MG-samples in the hydrogen analyzer, the transformation and crystallization occur. However, these do not affect the total amount of desorbed hydrogen (the hydrogen absorption capacity). Hcp-TiAl and \( a\)-TiAl absorb hydrogen of the amounts of 0.36 and 0.41 (H/M), respectively. We can’t discuss in details on the shape of TDS in the high temperature region, because the phase transformation occurs during heating. \( T_d \) for hydrogenated
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Fig. 5 TDS of hydrogenated hcp-TiAl and α-TiAl alloys.

Fig. 6 Hydrogen absorption capacities (CH) of hcp- and α-TiAl. (a) is the as-milled sample and (b) is the sample exposed to air before hydrogenation.

Fig. 7 XRD patterns of Ti0.40Al0.60 mechanically ground for selected times in 0.2 MPa argon.

**T**i0.50Al0.50H0.36 and α-Ti0.50Al0.50H0.41 is 853 K and 888 K, respectively. Generally, peaks in TDS correlate with hydrogen atoms desorbing from various sites which have different bonding energies, the larger the bonding energy, the higher the position of the peak in temperature. Since TDS of both alloys show nearly same onset temperature of hydrogen desorption and nearly same temperature dependence, it is suggested that local environments around hydrogen atoms are nearly same in both alloys. Of course, the long-range arrangements of the metal atoms are quite different in both alloys. The present work clearly demonstrates that original stoichiometric L10-TiAl does not absorb hydrogen, but the metastable TiAl phases, i.e. hcp-TiAl and α-TiAl prepared by MG can absorb hydrogen of the amount of 0.4 (H/M).

Figure 6 shows the hydrogen absorption capacity C_H of (a) MG–TiAl (not-exposed to air) and of (b) one exposed to air for 60 s. Although original L10-TiAl does not absorb hydrogen (not shown), both hcp-TiAl and α-TiAl prepared by MG absorb hydrogen of about 0.4 (H/M) when they are not exposed to air. If they are exposed to air before hydrogenation, their hydrogen absorption capacity drastically decreases. Consequently, a fresh surface is essential for hydrogen absorption for MG–TiAl. The important role of a fresh surface on hydrogen absorption rate has been pointed out for MG–FeTi, MG–LaNi5 and so on.1,8

(b) Ti0.40Al0.60

Figure 7 shows XRD patterns of off-stoichiometric alloyed Ti0.40Al0.60 powder mechanically ground for selected times in 0.2 MPa Ar. Ti0.40Al0.60 takes also an L10 structure. The Bragg peaks of the samples mechanically ground for 72 and 288 ks disappear and are replaced by the broad peak of an amorphous phase. The Bragg peaks of the hcp phase are observed after MG for 432 ks. These Bragg peaks are replaced with a broad maximum of an amorphous phase after MG for 1080 ks. That is, a cyclic crystalline amorphous transformation occurs in the same ways as TiCo.9,10

The sequence of the structural change of Ti0.40Al0.60 by
MG is expressed as follows.

\[ L_{102}^{-}\text{TiAl}(T_{i0.40}A_{i0.60}H_{0.19}) \rightarrow a^{-}\text{TiAl} \rightarrow \text{hcp-TiAl} \rightarrow a^{-}\text{TiAl} \quad (2) \]

Figure 8 shows TDS of hydrogenated hcp-\(T_{i0.40}A_{i0.60}H_{0.19}\) and \(a^{-}\text{TiAl}\). Hydrogen of the amounts of 0.21 and 0.19 (H/M) is absorbed in hcp-\(T_{i0.40}A_{i0.60}H_{0.19}\) and \(a^{-}\text{TiAl}\), respectively. Since TDS of hcp-\(T_{i0.40}A_{i0.60}H_{0.19}\) is sharper than that of \(a^{-}\text{TiAl}\), it is suggested that hydrogen atoms in the crystalline alloys occupy the sites with a narrower distribution width of the energy. \(T_{d}\) for hcp-\(T_{i0.40}A_{i0.60}H_{0.19}\) and \(a^{-}\text{TiAl}\) is 830 K.

(c) TiAl₂

Figure 9 shows XRD patterns of alloyed TiAl₂ powder mechanically ground for selected times in 0.2 MPa Ar. The Bragg peaks of the original sample are indexed on the basis of TiAl₂. After MG for 43 ks or more, the Bragg peaks of fcc-TiAl₂ are observed in the XRD patterns. No formation of an amorphous phase is observed in good agreement with the previous report.⁶ The sequence of the structural change of TiAl₂ by MG is expressed as follows

\[ D0_{22}^{-}\text{TiAl₂} \rightarrow \text{fcc-TiAl₂} \quad (4) \]

No hydrogen absorption is detected in this metastable fcc-TiAl₂.

4. Discussion

It has been reported that the hcp solid solution is formed for Al concentrations up to 60 mol% and the fcc solid solution is formed for 75 mol% Al by mechanical alloying (MA) of elemental Ti-Al powder blends.⁶ In addition, hcp-TiAl and fcc-TiAl are formed by MG of TiAl and TiAl₃, respectively, but no amorphous phase is formed.⁶ On the contrary, the present results clearly show that hcp- and \(a^{-}\text{TiAl}\), fcc- and \(a^{-}\text{TiAl₂}\) and fcc-TiAl₂ are formed by MG of TiAl, TiAl₂ and TiAl₃, respectively. No amorphous phase is formed for TiAl₃ in good agreement with the previous report.⁶ The phase formation can be explained by considering the relative stability of the respective phases in the Ti-Al system.

Figure 11 shows the free energy curves of the Ti–Al system calculated by the CALPHAD method.⁶ From this diagram, it can be seen that the hcp and fcc phases have minimal free energy if the intermetallic phases can’t be formed, while the amorphous phase has a higher free energy for all composition.
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Fig. 10 XRD patterns of TiAl3 mechanically ground for selected times in 0.2 MPa argon.

Fig. 11 Free energy curves at $T = 573$ K of stable and metastable phases in the Ti–Al alloys calculated by the CHALPHAD method.

In particular, the free energy of the amorphous phase for TiAl3 is higher. Therefore, it is difficult to obtain α-TiAl3 by MG. Thus, the formation of the hcp and fcc phases by MG of Ti-aluminides are explained by considering the relative stability of the respective phases. The formation of α-TiAl and α-TiAl2 after long MG is understood from these free energy curves.

Figure 12 shows hydrogen absorption capacity $C_{H}$ (H/M) and 50% hydrogen desorption temperature $T_d$ of the binary Ti–Al system hydrogenated at room temperature at 5 MPa $H_2$ pressure for 173 ks, and TiAl, Ti$_{0.40}$Al$_{0.60}$, TiAl2 and TiAl3 mechanically ground, which are unexposed to air, and hydrogenated at room temperature at 5 MPa $H_2$ for 86 ks.

are quoted from the references. Pure Ti absorbs hydrogen of 2.2 (H/M). $C_{H}$ of the Ti–Al alloys, prepared by arc melting and then pulverized, is reduced with increasing Al concentrations. No hydrogen is absorbed in the alloys for Al = 45 mol% and more. $T_d$ falls with increasing Al concentrations till Al = 20 mol%, but rises from 20 to 40 mol%Al in contrast to the simple and rough estimation of us. This rising of $T_d$ has been reported to result from the formation of amorphous alloys. $T_d$ in metastable Ti–Al prepared by MG falls with increasing Al concentrations. Although original TiAl (Ti$_{0.50}$Al$_{0.50}$ and Ti$_{0.40}$Al$_{0.60}$) and TiAl2 do not absorb hydrogen, hcp- and α-TiAl, and fcc- and α-TiAl3 prepared by MG absorb hydrogen of the amounts of 0.4 – 0.1 (H/M). The present work clearly demonstrates that MG is a useful technique for an emergence of the hydrogen absorption ability of intermetallic compounds containing much hydride-forming elements. $C_{H}$ (H/M) and $T_d$ of the MG–Ti–Al alloys is reduced and falls, respectively, with increasing Al concentration.

5. Summary and Conclusions

The transformation of L10–TiAl (Ti$_{0.50}$Al$_{0.50}$ and Ti$_{0.40}$Al$_{0.60}$), TiAl2 and D022–TiAl3 by mechanical grinding (MG) in an argon atmosphere have been investigated in order to study the stability of Ti-aluminides during the milling process. In addition, hydrogen absorption and desorption properties of the MG-alloys have been investigated. It has been made clear that mechanical grinding (MG) of TiAl, TiAl2 and TiAl3 gives rise to the formation of hcp- and amorphous (α-) TiAl, fcc- and α-TiAl2 and fcc-TiAl3, respectively. The formation of these metastable phases is reasonably explained by considering the relative stability of the respective phases cal-
culated by the CHALPHAD method. Although original Ti-aluminides do not absorb hydrogen at the pressure of 5 MPa at room temperature, hcp- and $\alpha$-TiAl, and fcc- and $\alpha$-TiAl$_2$ having a fresh surface absorb hydrogen of the amounts of $0.4 - 0.1$ (H/M). The present work clearly demonstrates that MG is a useful technique for an emergence of the hydrogen absorption ability of intermetallic compounds containing much hydride-forming elements.

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