Hydrogen Absorption and Desorption Properties of Ti₃Al–Ni Alloys *1

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Structures of as-cast and homogenized Ti_{75-x}Al_{25}Ni_x alloys before and after hydrogenation, the hydrogen content and the hydrogen desorption temperature of the hydrogenated Ti_{75-x}Al_{25}Ni_x alloys were investigated by a powder X-ray diffractometer (XRD) and a hydrogen analyzer. The hydrogen content of these alloys decreased with increasing Ni content, and was almost independent of the hydrogenation temperature and the structure of the alloys, but 50% hydrogen desorption temperature, T_d, varied widely with them. The formation of amorphous phases raised T_d. On the contrary, a drop in T_d was achieved by hydrogenation of a mixture alloy of the D0_{19} and C14 Laves phases.

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1. Introduction

In recent years, novel hydrogen storage materials having a large hydrogen capacity are strongly desired.1) D0_{19}–Ti₃Al is one of the potential hydrogen storage alloys because of its lightweight and a large hydrogen absorption capacity more than 3 mass%.2) However, Ti₃AlH_x is too sable, i.e. its hydrogen desorption temperature is too high to use for practical applications. Then, it is necessary and important to reduce its hydrogen desorption temperature. Recently, the present authors investigated the effect of substitutional elements on hydrogen absorption-desorption properties of Ti_{75-x}Al_{25}M_x (x = 15 and 25 mol%) alloys.3, 4) Among the alloying elements, Mn, Co, Nb and Ni have an ability to reduce the hydrogen desorption temperature. However, it is still uncertain what factor controls a drop in the hydrogen desorption temperature of Ti_{75-x}Al_{25}M_xH_y. In the present work, the effect of Ni addition on the crystal structures of Ti₃Al before and after hydrogenation, the hydrogen content and the hydrogen desorption temperature of (Ti₃Al–Ni)H_x alloys are investigated.

2. Experimental

Ti_{75-x}Al_{25}Ni_x (x = 0, 5, 10, 15, 20, 25, 30, 35 mol%) alloys were prepared by arc melting under an argon atmosphere. The ingots were homogenized at 1073 K for 605 ks in vacuum of 3.0 × 10⁻³ Pa and then water quenched. They were pulverized and passed through the 50 mesh sieve. After an activation treatment of samples at 673 K for 3.6 ks in vacuum of 3 Pa, they were reacted with high purity (7N) hydrogen of 5 MPa for 86 ks. Structures of samples before and after hydrogenation were identified with a powder X-ray diffractometer (XRD) using CuKα radiation monochromated by graphite. The amount of absorbed hydrogen and thermal desorption spectrum (TDS) were measured by a hydrogen analyzer. Hydrogenated samples were thermally analyzed with a differential scanning calorimeter (DSC) under an argon flow atmosphere.

3. Results and Discussion

Figure 1 shows XRD patterns of as-cast (a) and homogenized (b) Ti_{75-x}Al_{25}Ni_x alloys. As-cast and homogenized Ti₃Al and Ti_{70}Al_{25}Ni_5 alloys take the D0_{19} structure. As-cast Ti_{60}Al_{25}Ni_{15} and Ti_{90}Al_{25}Ni_{35} alloys consist of a mixture of D0_{19} and C14 phases. As-cast Ti_{40}Al_{25}Ni_{35} is a single-phase alloy with the C14 Laves structure. Homogenized-Ti_{60}Al_{25}Ni_{15}, -Ti_{50}Al_{25}Ni_{25} and -Ti_{40}Al_{25}Ni_{35} alloys consist of a mixture of the D0_{19} and L2₁ phases.

Figure 2 shows a part of the isothermal section of the ternary Ti–Al–Ni phase diagram at 1073 K.5) Small open circles denote the compositions of alloys investigated in the present work. Three phases, i.e. TiAlNi_2 (the L2₁

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NiTi (Ni), AlNi, TiAl (D0₁₉), Ti₂Ni, TiNi, TiNi₃, TiAl₂Ni (L₂₁), Ti₂Al₃Ni (C₁₄ Laves), and Al₂Ni₁₂ are formed as a ternary single-phase. According to this diagram, Ti₇₅₋ₓAl₂₅Niₓ alloys are expected to consist of the D₀₁₉ and L₂₁ phases. In fact, the homogenized samples consist of these two phases (Fig. 1(b)), but the as-cast ones consist of a mixture of the D₀₁₉ and C₁₄ Laves phases (Fig. 1(a)). Then, the C₁₄ Laves and the L₂₁ phase is a metastable and an equilibrium one, respectively.

Figure 3 shows XRD patterns of as-cast (a) and homogenized (b) Ti₇₅₋ₓAl₂₅Niₓ alloys hydrogenated at room temperature. Bragg peaks of the hydrogenated C₁₄ Laves phases shift to the lower angle side keeping the original structure, indicating the formation of a solid solution with hydrogen. On the other hand, the L₂₁ phase does not absorb hydrogen, because no shift of the Bragg peaks is observed.

Figure 4 shows XRD patterns of as-cast (a) and homogenized (b) Ti₇₅₋ₓAl₂₅Niₓ alloys hydrogenated at 473 K. These XRD patterns indicate that binary and ternary D₀₁₉–Ti₃Al–Ni alloys change to the fcc type (Ti, Al)H₂. The ternary C₁₄ Laves phase absorb hydrogen forming a solid solution, but the ternary L₂₁ ones do not absorb hydrogen.

Figure 5 shows the relation between the hydrogen content (H/M) and the Ni content in the as-cast and homogenized Ti₇₅₋ₓAl₂₅Niₓ alloys hydrogenated at room temperature and 473 K. In this figure, (a), (b), (c) and (d) denote the states of the alloys and the hydrogenation temperature. Existing ranges of the hydrogenated phases are also shown in the lower part of this figure. The hydrogen content decreases monotonously with increasing Ni content, and is almost independent of the temperature and the structures of the alloys before and after hydrogenation. It is worth noticing that the hydrogen content is determined only by the amount of Ni, i.e. the amount of Ti in the alloys.

Figure 6 shows the relation between the 50% hydrogen desorption temperature T_d and the Ni content in the as-cast and homogenized Ti₇₅₋ₓAl₂₅Niₓ alloys hydrogenated at room temperature and 473 K. In the present work, T_d was defined as the temperature where the half of absorbed hydrogen is desorbed. (a), (b), (c) and (d) denote the same meanings of them in Fig. 5. The open symbols denote amorphous hydride. We can see that T_d depends on the Ni content, the hydrogenation temperature and structures of the alloys before and after hydrogenation.
4. Summary and Conclusion

The ternary C14 Laves and L2₁ phases were formed coexisting with the ternary D₀₁₉−Ti₃Al−Ni one in the as-cast and in the homogenized Ti₇₅₋ₓAl₂₅Niₓ alloys, respectively. The binary D₀₁₉−Ti₃Al became amorphous by hydrogenation independent of the temperature, while the ternary D₀₁₉−Ti₃Al−Ni alloys became amorphous and fcc type hydride by hydrogenation at room temperature and 473 K, respectively. The C₁₄ Laves phase absorbed hydrogen forming the solid solution, but the L₂₁ phase did not absorb hydrogen. The hydrogen absorption capacity decreased with increasing Ni content, and was almost independent of the hydrogenation temperature and structures of the alloys before and after hydrogenation. On the contrary, the 50% hydrogen desorption temperature T₃ varied widely with them. The formation of an amorphous phase raised T₃. On the contrary, hydrogenation of the C₁₄ Laves + D₀₁₉ phases gave rise to a drop in T₃.

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