Protium Absorption Properties of La–TM–Si (TM = Co, Ni) Ternary Intermetallic Compounds

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The protium-absorbing characteristics such as the amount of absorbing protium and the hydrogen reaction have been studied for the LaTMSi, LaTMSi and LaTM2Si2 (TM = Co, Ni) ternary intermetallic compounds. For these compounds, it is found from DSC measurements that only the LaCoSi and LaNiSi compounds show hydride reactions at elevated temperatures. The LaCoSi alloy has a disproportionation reaction at 457 K, whereas the LaNiSi alloy reversibly absorbs and desorbs protium near 425 K. The maximum absorbed amount of protium is 0.52 mass% for the LaNiSi alloy.

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I. Introduction

A LaNi₅ intermetallic compound is a well-known hydrogen storage material, and is presently used as the negative electrode in the Ni-Metal Hydride secondary battery. Intensive research for improvements of LaNi₅ compounds as a negative electrodes has produced Ni-MH batteries whose capacity is twice that of Ni-Cd batteries, and is almost comparable to Li-ion batteries. The electrocapacitance of the LaNi₅ electrode has nearly reached a limit at present.

The high demand for increased capacity of secondary batteries for Electric Vehicles (EV) has stimulated researchers to develop new metal-hydrides such as Mg-Ni(7) or V-based bcc alloys(8,9). Most of the studies have been limited to the study of binary intermetallic compounds which appear in binary alloy systems. Few studies have been devoted to seeking ternary intermetallic compounds.

The purpose of the present study is to discover new hydrogen storage intermetallic compounds which appear only in ternary alloy systems. The studied compounds were chosen based on the following criteria: (1) rare-earth ternary intermetallic compounds with antiferromagnetism since the protium absorption properties of most of the reported compounds are unknown, and (2) the rare-earth content of the compounds are higher than that of LaNi₅ since there may be the possibility that the high rare-earth content may allow the absorption of higher amounts of protium. The chosen compositions in this study are LaTMSi, LaTMSi and LaTM2Si2 (TM = Co, Ni). The present paper describes the protium-absorption properties of these ternary intermetallic compounds.

II. Experimental Procedures

Ten-gram ingots were prepared by arc-melting 99.9% La, 99.5%Co, 99.97%Ni and 99%Si in an argon atmosphere. Several remeltings were employed to make the ingots homogeneous. Each ingot was annealed at 1273 K for 50 h for confirming the homogeneity of the ingots. The phases were analyzed using an X-ray diffractometer (XRD) with Cu-Kα radiation. The hydrogen reaction temperatures were monitored with a differential scanning calorimeter (DSC), while heating from 373 to 743 K at a rate of 0.17 K/s under 2.5 MPa hydrogen pressure. The pressure-composition-iso therm (PCT) curves of the specimens were measured by a Sieverts-type apparatus at 313 K and at several hydrogen reaction temperatures which were determined from the DSC curves.

III. Experimental Results

1. La–Co–Si system

Figure 1 shows the X-ray diffraction patterns of LaCoSi, LaCoSi and LaCoSi samples after annealing at 1273 K for 50 h. The LaCoSi, LaCoSi, and LaCoSi compounds are supposed to show the Cu₃Sb, CeNiSi₂, ThCr₂Si₂ type structures, respectively. The diffraction patterns show that almost a single phase is formed in the alloys. Figure 2 shows the PCT curves of the LaCoSi, LaCoSi, and LaCoSi samples measured at 313 K. Among the three compounds, the LaCoSi sample absorbs the largest amount of protium, which is nearly 0.47 mass% protium at 7.2 MPa hydrogen pressure. The hydrogen reaction temperature was determined by DSC analysis. The DSC curve of a LaCoSi alloy is shown in

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Fig. 1 X-ray diffraction patterns of LaCoSi, LaCoSi2, and LaCo2Si2 samples annealed at 1273 K for 50 h.

Fig. 2 PCT curves of LaCoSi, LaCoSi2, and LaCo2Si2 samples measured at 313 K.

Fig. 3 Two exothermic peaks appear. Sharp and small exothermic peaks are observed at 457 and 563 K, respectively, although both the LaCoSi2 and LaCo2Si2 compounds show no peaks in the DSC curves.

Figure 4 shows the PCT curves of the LaCoSi alloy measured at the exothermic temperatures of 457 and 563 K. The protium content in the compounds from two curves is nearly independent of hydrogen pressure, and is about 0.45 mass% based on both curves. In order to determine what types of hydride reactions occurred at these temperatures, the phases were studied using X-ray diffraction analysis after absorbing the protium at 457 and 563 K. Figure 5 shows the diffraction patterns of the LaCoSi alloy before and after hydriding at 457 and 563 K. After hydriding, the alloy consists of the LaCo13, LaH2 and Cu2Sb phases, which means that the LaCoSi compound partially decomposes into LaCo13 and LaH2 by absorbing protium. Therefore, it is considered that the hydride reaction at 457 K is a disproportionation reaction.

2. La–Ni–Si system

Figure 6 shows the X-ray diffraction patterns of the
LaNiSi, LaNiSi$_{2}$ and LaNi$_{5}$Si$_{2}$ samples after annealing at 1273 K for 50 h. The LaNiSi compound with a LaPtSi$_{2}$-type structure is obtained as an almost single phase, whereas the LaNi$_{5}$Si$_{2}$ and LaNi$_5$Si$_2$ phases, which belong to the CeNi$_{5}$Si$_2$ and ThCr$_2$Si$_2$ type structure, respectively$^{[13]}$, are found to be the main constituents of the alloys, although very small amounts of an undefined phase were also observed. The amount of absorbing protium at 313 K for these compounds was investigated. Figure 7 shows the PCT curves of the LaNiSi, LaNiSi$_{2}$ and LaNi$_5$Si$_2$ samples measured at 313 K. The LaNiSi sample shows the highest amount of absorbed protium which is nearly 0.46 mass% at 7.2MPa hydrogen pressure.

The protium-absorption behavior of these compounds between room temperature to 743 K was then examined. The LaNi$_5$Si$_2$ and LaNi$_5$Si$_2$ alloys show no hydride reaction over this temperature range in the DSC curves. However, the LaNiSi alloy exhibits exothermic peaks near 425 and 726 K as shown in Fig. 8. The peak around 726 K is not obvious. Figure 9 shows the X-ray diffraction patterns of the LaNiSi alloy before and after hydriding at 563 K which is considered to complete the exothermic reaction. Both patterns are nearly the same, but the lines in the after-hydriding pattern slightly shift toward low angles in comparison with that before hydriding. This means a lattice expansion by absorbing hydrogen. The lattice constants calculated from both patterns are: (1) before hydriding: $a=0.4183$ and $c=1.4081$ nm, (2) after hydriding: $a=0.4188$ and $c=1.4222$ nm. It is considered that the remaining hydrogen in the lattice at 0.1 MPa causes this expansion. As the LaNiSi phase does not decompose, this hydride reaction is found to be a protium absorbing reaction. The absorbed amounts of protium by the LaNiSi compound was measured at 563 K. Figure 10 shows the PCT curves of the LaNiSi alloy after the 1st to 3rd absorption-desorption cycles at 563 K. It is seen that the LaNiSi alloy reversibly absorbs and desorbs protium. However, the total amount of protium is limited to nearly 0.52 mass% at 5.6 MPa hydrogen pressure.
IV. Conclusions

The protium-absorbing properties such as the hydrogen reaction temperatures and the amount of absorbing protium of the LaTMSi, LaTMSi$_2$ and LaTM$_2$Si$_2$ (TM = Co, Ni) alloys were studied. There are no peaks during heating from 373 to 733 K in the DSC curves for the LaTMSi$_2$ and LaTM$_2$Si$_2$ (TM = Co, Ni) alloys, but absorption peaks are observed for the LaCoSi and LaNiSi alloys. At elevated temperatures, the LaCoSi and LaNiSi alloys show hydride reactions such as the disproportionation reaction at 457 K and the absorption and desorption of protium near 425 K. The maximum absorbed amount of protium is 0.52 mass% for the LaNiSi alloy.

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