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Laves Phase $\text{CaAl}_{2-b}\text{X}_b$ Alloys with Substitutional and Interstitial Elements X

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Introduction

Metal hydrides are promising media for the storage and transportation of a great amount of hydrogen. Various alloys and carbon materials have been developed for these purposes [1,2]. However, hydrogen storage in the form of a metal hydride has not reached commercial viability. For their practical application to this technological field, the development of inexpensive alloys with large hydrogen capacities is considered to be one of the primary requirements.

Binary Laves phase alloys with the MgCu_2 -type structure such as RENi_2 and ZrV_2 are known to absorb a large amount of hydrogen, forming hydrides with H/M atomic ratios larger than 1.0 [2]. Calcium and aluminum, which are lighter and cheaper than constituent metals of other hydrogen storage alloys, also form the MgCu_2 -type compound CaAl_2 [3] as illustrated in Figure 1. The CaAl_2 offers the possibility of high hydrogen storage capacity with extraordinary low material cost. However, CaAl_2 does not absorb as much hydrogen at near room temperatures [4], probably because, according to the Westlake's empirical law, the distance between interstitial sites (T-sites) for hydrogen atoms is too large for simultaneous occupation of hydrogen to form an unstable hydride. It was thought that the lattice constant, 0.8040(2) nm [5], of CaAl_2 should be reduced because it is much larger than those (about 0.725 nm) of other hydrogen storage alloys with MgCu_2 -type structure. In this project, addition of substitutional and interstitial elements X has been attempted. It was considered important to control the lattice parameters in order to change some characteristics, since the Laves phase alloys, such as CaAl_2 , are often called "size factor compounds". On the other hand, the CaAl_2 alloy was disproportionated into CaH_2 and Al irreversibly at high temperatures [6]. It is also important to prevent the CaAl_2 alloys from disproportionation during hydrogenation.

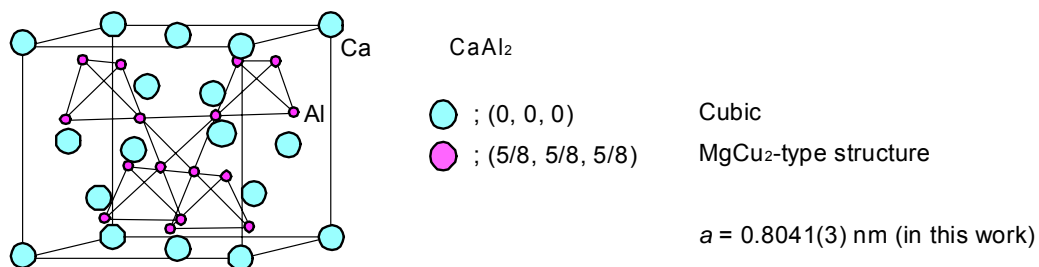


Figure 1 - Crystal structure of CaAl₂

The phase diagram of the Ca-Al binary system is available in the literature [7]. In addition, Ca and/or Al in CaAl₂ can be substituted partially by other elements with the Laves phase structure, as reported in CaLi_yAl_{2-y} ($0 \leq y \leq 2$) alloys [8]. However, there is no available information on whether hydrogen atoms can occupy the sites in the crystal cells of the CaAl₂-based alloys, that is have hydrogenation and dehydrogenation characteristics.

In this project, modification of Laves phase CaAl₂-based alloy by partial substitution of interstitial elements by X was attempted to improve the hydrogenation characteristics [9] and to suppress disproportionation. In particular, B and Si were chosen as the element X because the CaAl₂ alloys containing transition metals as X did not form the Laves phase structure but precipitated secondary phases immediately. The substitutions B and Si are upper and right neighbor elements of Al on the periodic table, respectively.

Experimental Work

The following collaborative work was carried out in order to prepare experimental Ca-Al-based alloys and analyze their metallographic and hydrogenation characteristics: Calcium (99.9% purity), aluminum (99.9%), boron (99.5%), silicon (99.9995%) and some other metals such as nickel, palladium and tin were used to prepare samples. A binary alloy CaAl₂ was synthesized by radio-frequency induction melting in an alumina crucible in a 0.1 MPa atmosphere of argon (99.998%). The exact composition of the obtained alloy was Ca:Al = 1:2.08, per analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES). This CaAl₂ alloy was used for characterization and as a seed material to synthesize the derivative alloys. In most cases, the other samples were prepared by melting like the CaAl₂. Sometimes, preliminary Al_{2-b}X_b alloys were prepared before CaAl_{2-b}X_b alloys were synthesized. Some Si-containing alloy samples were prepared by sintering in a 0.1 MPa atmosphere of argon (99.998%).

Metallographic structure was observed with a scanning electron microscope (SEM). The compositions of observed grains and regions in alloys were measured by wavelength dispersion X-ray analysis (WDX). Crystal structures and lattice parameters of the alloy samples were determined by powder X-ray analysis with CuK α radiation using a diffractometer with the CuK α ₁ radiation monochromated strictly [10,11] using a Guinier-Hägg focusing camera. The thermal stability and hydriding behavior of the alloys were preliminarily examined by differential thermal analysis (DTA) over the temperature range from room temperature to 400°C in two separate kinds of atmospheres: 3 MPa argon (99.998%) and 3 MPa hydrogen (99.9995%) of 3 MPa. Analysis in the former atmosphere was performed in order to check phase transition of the sample alloy itself under high temperature and pressure.

P-C isotherms of the alloys were measured by use of Sieverts' apparatuses at temperatures from 40 to 200°C under hydrogen pressures from 1 kPa to 3 MPa. Before measurement of the P-C isotherms, initial activation treatments of the alloys were carried out through the following procedures: 1) the alloy powder (about 0.30 g) was placed in a high-pressure reactor (about 3

cm³) and heated up to 350°C under evacuation by a rotary and a turbomolecular pump and 2) the alloy was hydrogenated at a hydrogen pressure of 3 MPa at 200°C for 2 hours and dehydrogenated by evacuation at 300°C for 2 hours.

F-treatments were attempted in order to improve the surface of the alloys because it was found by X-ray photoelectron spectroscopy (XPS) that this series of samples are covered with a thick oxide layer.

Results and Discussion

The basic alloy CaAl₂ (CaAl_{2.08}, exactly) that was prepared in this work consisted of exactly two phases: CaAl₂ main phase, with a cubic MgCu₂-type structure $a = 0.8041(3)$ nm [9,12,13,14], and CaAl₄ secondary phase, with tetragonal BaAl₄-type structure. CaAl₂ did not absorb and desorb hydrogen practically at near room temperature through a direct reaction between solid (CaAl₂) and gas (H₂) phases, as is expected from Reference [8].

In this work, apparent substitutions of Al by B and/or Si in CaAl_{2-b}(B, Si)_b were investigated preferentially to control the lattice cell size. Although some other metal elements were also attempted as substitutions for Al in CaAl₂, the added elements made the alloy decompose into CaAl₂ phase and any other phases that did not hydrogenate. As a result, the added elements did not substitute into the matrix, i.e., no homogeneous intermetallic phase with the Laves phase structures was formed.

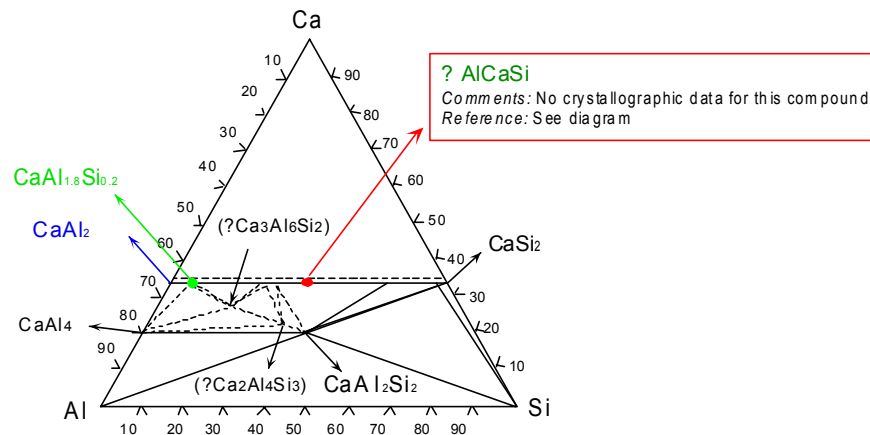


Figure 2 - Isothermal section of Ca-Al-Si ternary system at 400°C

As a next step, the X-element was substituted to a larger fraction of Al in the CaAl₂ alloy in order to search for new intermetallic compound phases that can absorb and desorb hydrogen. In this work, the Ca-Al-M ternary alloys in which Si was chosen as M were investigated primarily relative to their crystal structure and hydrogenation characteristics. In the Ca-Al-Si ternary system, unexplored regions still remained although only a ternary isothermal section at 400°C is available, as shown in Figure 2 [15]. The b value in CaAl_{2-b}Si_b was gradually increased from 0 to 1. When $b = 0.2$, as observed by SEM and WDX, the CaAl_{1.8}Si_{0.2} alloy consisted of two phases - matrix and a secondary phase at grain boundaries. The matrix phase in CaAl_{1.8}Si_{0.2} (as well as CaAl₂ itself) was crystallized in the MgCu₂-type structure with a composition close to Ca:Al = 1:2. Its lattice constant was very similar to CaAl₂. The composition of the boundary phase was Ca:Al:Si = 1:1:1. The crystal structure of the boundary phase was identified as hexagonal, AlB₂-type by Guinier-Hägg XRD. Thus, the CaAlSi phase in CaAl_{1.8}Si_{0.2} alloy was crystallized in a hexagonal AlB₂-type structure as shown in Figure 3: $a = 0.4210(6)$ nm, $c = 0.4425(8)$ nm [16,17]. This substance, CaAlSi, should be regarded as a new intermetallic compound because it was

published in neither the crystallographic data, such as Joint Committee of Powder Diffraction Standards' (JCPDS) cards, nor metallurgical data, such as the ternary alloy phase diagrams.

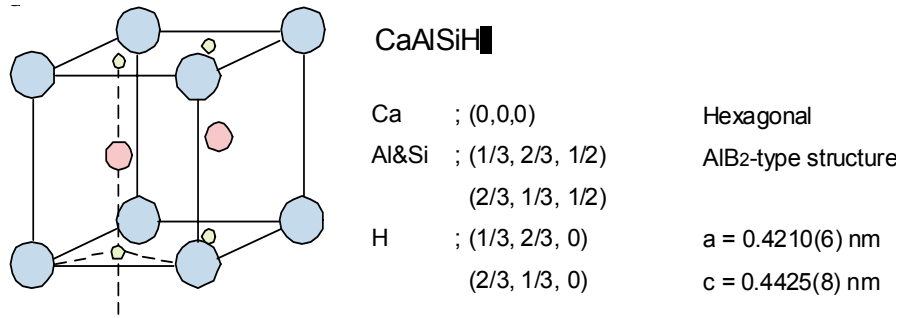


Figure 3 - Crystal structure of CaAlSi and the expected positions occupied by H atoms. The positions of H atoms were analyzed with those of ZrBe₂ and ThNi₂, which are hydrogen storage alloys with hexagonal AlB₂-type structure.

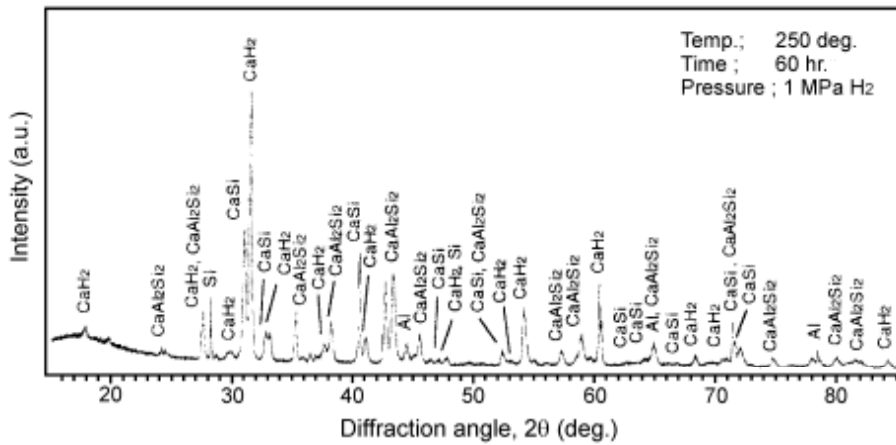


Figure 4 - Guinier-Hagg XRD profile of CaAlSi (with CaAl₂Si₂) after disproportionation

Hydrogen storage characteristics of the new intermetallic compound CaAlSi were investigated. We attempted to synthesize a sample containing the CaAlSi as a main phase in order to examine its hydrogenation characteristics more precisely. It was not easy to directly synthesize the homogeneous CaAlSi and its hydride samples by melting or sintering of a mixture of CaH₂, Al and Si powders. The CaAlSi phase was formed as the main phase in an alloy with an overall composition of CaAl_{1.8}Si, prepared by sintering of a mixture of CaAl_{1.8}Si_{0.2} and Si powders in an Ar atmosphere. A CaAl₂Si₂ intermetallic compound was formed as a secondary phase. The CaAlSi phase in the CaAl_{1.8}Si sample disproportionated irreversibly at temperatures above 250°C as shown in Figure 4; however, this was not the case for CaAl₂Si₂. Crystallinity of the CaAlSi phase declined without expansion or contraction of the lattice cell during hydrogenation. The phase disproportionated even at temperatures below 200°C. The results from XRD analysis in a hydrogen atmosphere of 3 MPa and 250°C suggested the following disproportionation process:



In this case, it was considered that the disproportionation process was indifferent to the CaAl_2Si_2 phase present and did not complete itself because of restraints imposed by the Gibbs phase rule.

Surface analysis of air-exposed $\text{CaAl}_{1.8}\text{Si}_{0.2}$ by XPS showed a thick oxide/hydroxide layer. Surface treatment of the same alloy with fluoride-containing solutions were attempted to remove that layer, but the alloys did not hydrogenate. The alloy seemed to be very sensitive to moisture and oxygen.

The P-C isotherms for $\text{CaAl}_{2-b}\text{Si}_b$ were poor due to continuous disproportionation and irreversibility and are, thus, not reported here.

Conclusion

Improvement of the hydrogenation properties of the CaAl_2 Laves phase alloy has been investigated by partial substitution of typical elements for Al in order to find lighter and cheaper hydrogen storage alloys. In particular, B and Si as substituents X in $\text{CaAl}_{2-b}\text{X}_b$ were investigated in this work. However, they had little impact on the hydrogenation characteristics of the matrix and were not very effective in the control of the lattice parameters of the Laves phase, rather formed secondary phases. While a new phase CaAlSi was found through this work, new phases that absorb and desorb hydrogen reversibly were not found in the investigated CaAl_2 -based alloys.

As a result of this project, it was suggested that the above-mentioned alloys such as Ca-Al-Si ternary systems do not achieve the targets of the IEA Task 12. However, it was also suggested that there should be a lot of unknown phases worthy of further investigation.

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