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Ca-based Ternary Alloys

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Introduction

The ternary $CaAl_{2-b}X_b$ (X = Al, B and Si) alloys studied in Project No. 4 did not have homogeneous structures, but rather had a matrix with the Laves phase $MgCu_2$-type structure and secondary phases. As for hydrogenation characteristics, all phases did not absorb and desorb hydrogen reversibly. Instead they disproportionated to form CaH_2 in the hydrogenation process at about 250°C, as shown in Ref [1] and the Project No. 4 chapter of this Final Report for IEA Task 12. Most of "hydrogen storage alloys" contain 3d transition metals as major constituent elements. For Ca-based intermetallic compounds, $CaNi_2$, $CaNi_3$ and $CaNi_5$ form their corresponding hydrides [2-8]. Taking this fact into account, it is suggested that the $CaAl_{2-b}X_b$ alloys that contain no transition metals do not reversibly absorb and desorb hydrogen. Transition metals on the surface of the alloys are expected to work as useful catalysts to accelerate hydrogenation and dehydrogenation. In addition, it is possible that some undiscovered intermetallic compound phases remain in Ca-Al-transition metal ternary systems. The objective of this project was to search for new reversible hydrides of ternary alloys consisting of 3d transition metals and cheap and light metals such as Ca, Mg and Al. This project was exploratory and limited to a preliminarily experimental survey on possibilities for gaseous hydrogen storage. Taking the target for hydrogen storage capacity into account, 3d transition metals were evaluated as third elements in ternary Ca-Al-TM (TM; transition metals) alloys. In order to maximize the information about new compounds and hydrides as much as possible, alloys with the crystal structures in addition to Laves-phases type were also investigated.

In this project, the Ca-Al-based ternary alloys containing 3d transition elements such as Co, Ni and Cu were investigated.

Experimental Work

Calcium (>99.0 % purity), nickel (>99.0 %), cobalt (>99.0 %), copper (>99.7 %) and aluminum (>99.8 %) were used as starting materials.

The all Ca-Cu-Al alloy samples were prepared in a quartz tube crucible by radio-frequency induction melting under an Ar atmosphere (99.9995 %) of 67 kPa (500 Torr). It turned out that the samples were sometimes contaminated by a small amount of Si from the crucibles, as seen by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Molten Ca metal

reduced some quartz to Si during induction melting at high temperature. However, the contamination with Si did not influence formation of phases in the alloys as determined by powder XRD. The resultant samples were put into Mo foil boxes and annealed under an Ar atmosphere (0.6 Mpa) at low temperature (450°C) in order to avoid melting, due to the low eutectic temperature (485°C).

The ternary Ca-Ni-Al and Ca-Co-Al alloy samples were prepared by sintering methods under an Ar (99.9995 %) atmosphere (0.6 Mpa) and at 500 or 700°C in Mo foil boxes. In preparing these ternary alloys, $CaAl_{2.08}$ (see the Project No. 4 chapter) alloy powder was also used as a Ca source. Since the metallic Ca powder was not commercially available, the grain sizes of the ingredient powders should be as similar a size as possible for the preparation of the sample by sintering. Ca metal is easily vaporized. Therefore, the amount of metallic Ca granules was minimized. The starting materials were mixed with an agate mortar and pressed into pellets (9 mm diameter and about 5 mm height) in a mold under a mechanical pressure of 6.17 MPa (4 ton/cm^2) in a glove box filled with purified and dried Ar. The pellets were sintered at 700°C for 10 hours under an Ar atmosphere of 0.6 MPa.

Metallographic structure was observed with a scanning electron microscope (SEM, S-2500CX, Hitachi Manufacture Co., Ltd.). The compositions of the observed structure in alloys were measured by wavelength dispersion X-ray analysis (WDX, WDX-3PC by Microspec Co., Ltd.). In both cases, the acceleration voltage for the irradiating electron beam was 14 kV.

Crystal structures and lattice parameters of the alloy samples were determined by powder X-ray diffraction analysis with monochromated CuKα radiation using a diffractometer (XRD, RU-200, Rigaku Co., Ltd.). The tube voltage and current were 40 kV and 150 mA, respectively. The diffraction peak positions from samples were corrected with those from the external standard Si.

The thermal stability and hydriding behavior of the alloys were examined with a differential thermal analyzer (DTA, DSC8230HP, Rigaku Co., Ltd.) system from room temperature to below 500°C under two kinds of atmospheres: H_2 (99.99995 %) at 3 MPa and Ar (99.999 %) at 0.6 MPa. The sample pans used were Al or Pt and the reference was an active Al_2O_3. This examination was performed repeatedly through heating and cooling under the H_2 atmosphere in order to test stability of the formed phases.

Results and Discussion

As a preliminarily check before investigation of the Ca-Ni-Al ternary alloys, the hydrogenation characteristics of Ca-Ni binary multi-component alloys, $CaNi_{2.28}$ and $CaNi_{2.86}$ (annealed at 800°C for 10 hours), were examined using DTA and XRD. The alloys absorbed hydrogen immediately at near room temperature and they disproportionated irreversibly into CaH_2 and Ni. In the Ca-Ni-Al system Al was added into the Ca-Ni system in order to avoid disproportionation of Ca-Ni-based phases during reaction with hydrogen. The samples were sintered at 700°C and quenched in order to retain the phases present at the sintering temperature. The distribution of phases at 700°C was plotted on a ternary diagram with at least six regions, as shown in Figure 1. There were no new ternary intermetallic compound phases at 700°C, and the diagram was very similar to the phase relationships as described on an isothermal section at 500°C [9].

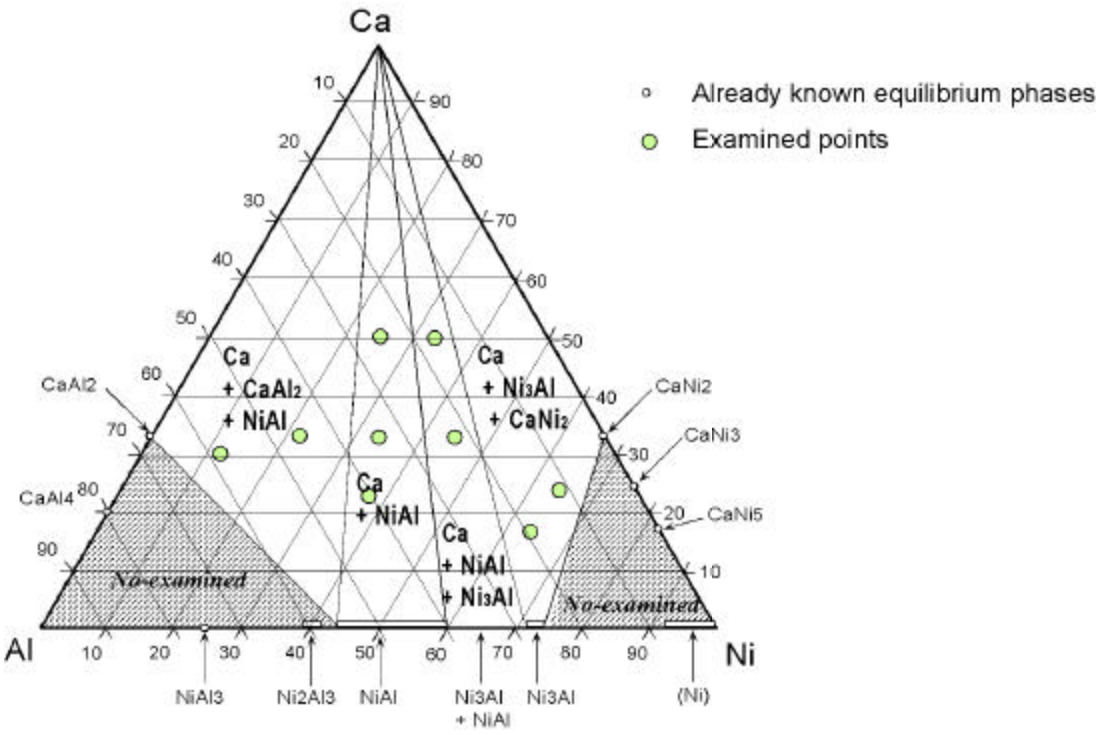

Figure 1 - Ternary diagram for the 700°C phase distribution in the Ca-Ni-Al system

An isothermal section of the ternary Ca-Co-Al system at 500°C [10], a partial phase diagram of binary Ca-Co system at only the Co-rich side [11] and full diagrams for the binary Ca-Al and Al-Co systems were already reported, but large unexplored regions remain in the Ca-Co-Al and Ca-Co systems. There is no further information on the phase relationships in these systems. In this work, the alloys with several kinds of compositions (Ca:Co:Al = 5:1:4, 2:1:1, 5:4:1, 3:2:5, 1:1:1, 1:2:2, 1:5:2 and 1:6:2) were investigated metallurgically using the sintering method. As a result of XRD and SEM/WDX, three regions, (Ca)+CoAl, (Ca)+(Co)+CoAl and (Ca)+$CaAl_2$+CoAl, could be drawn on a ternary triangle. Phase relationships in Ca-rich and Al-poor composition region could not be identified because many unknown peaks were observed in the XRD profiles and it was even very difficult to observe their metallographic structure by SEM/WDX. The phase relationship at 700ºC was plotted as the ternary diagram shown in Figure 2. However, this diagram at 700ºC was quite different from that at 500ºC [10]. However, there were no new phases at 700ºC as shown in the diagram.

For the Ca-Cu-Al system, the ternary alloys with compositions of Ca:Cu:Al = 4:1:1, 6:2:1 and 1:1:1, and the binary equilibrium phases, Ca_2Cu, CaCu and $CaCu_5$, were investigated for phase relationships. Nearly homogeneous (not single phase) samples were obtained through the induction melting method, and the matrix of the samples consisted of the phases as expected from and the reported phase diagrams at 500ºC [12]. Also in this system, phase relationships in the Ca-rich and Al-poor composition region could not be identified because many unknown peaks were observed in the XRD profiles and it was even more difficult to observe their metallographic structure by SEM/WDX. A provisional schematic diagram for this system is shown in Figure 3.

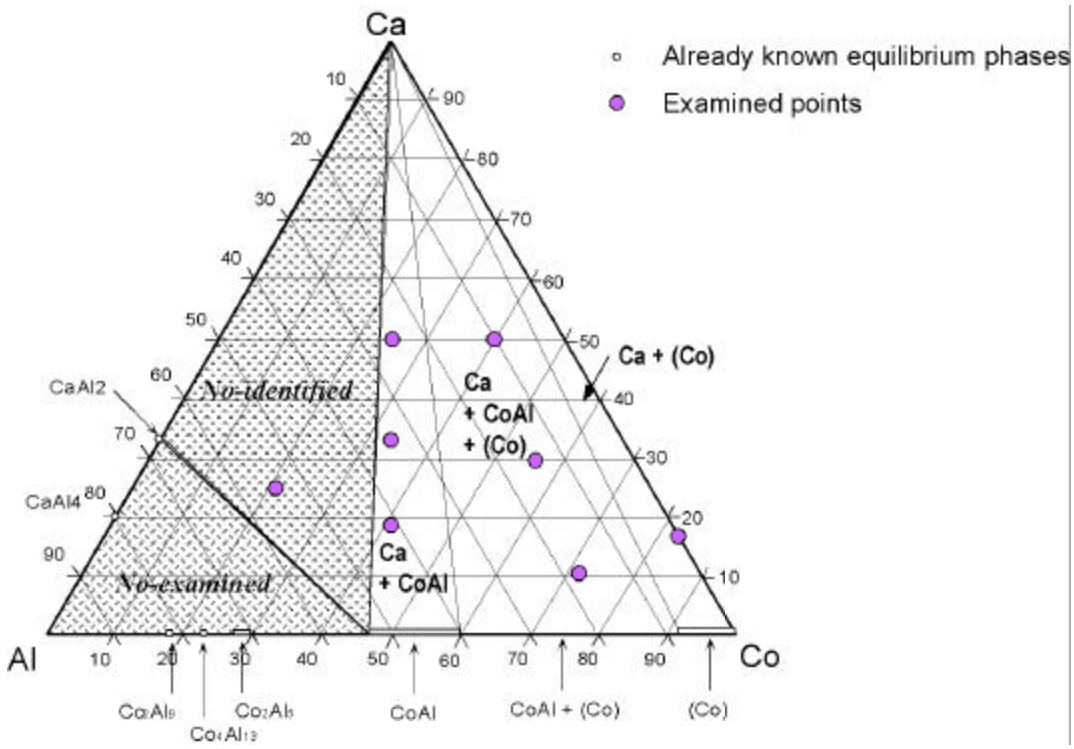

Figure 2 - Schematic diagram for phase distribution at 700°C for the Ca-Co-Al system

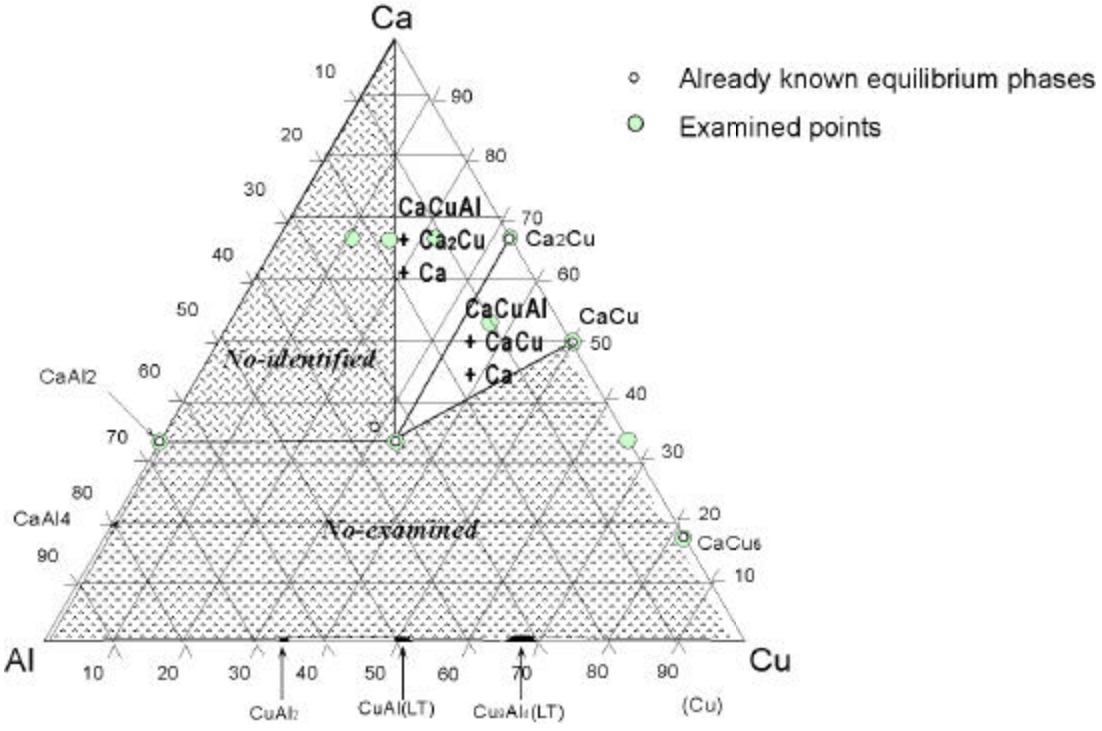

Figure 3 - Ternary diagram for phase distribution in the Ca-Cu-Al system

Hydrogenation tests for the Ca-Cu-Al alloy samples were performed by DTA and XRD. All the samples disproportionated irreversibly to form CaH_2 and Cu-Al compound phases during the first heating/cooling cycle under a hydrogen atmosphere of 3 MPa. However, the results of the repeated DTA suggested that decompositions of the ternary phases were slower than that of the Ca-Cu and Ca-Al binary system alloys. This may prove useful for designing new alloys.

For the Ca-TM-Al alloy samples investigated in this work, many "unidentified" X-ray diffraction peaks were observed without reproducibility, in particular in the samples with Ca-rich and Al-poor compositions. It was too difficult to identify the unknown peaks. It is reported that there are several non-equilibrium phases in the Ca-Al system and no information on their crystallographic data [13]. Additionally, handling and analyzing of the samples are very difficult because the alloys with Ca-rich compositions are very easily oxidized and hydrolyzed.

Conclusions

In this Project (a sequel to Project No. 4), Ca-based ternary alloys in the Ca-Ni-Al, Ca-Co-Al and Ca-Cu-Al systems were investigated relative to phases formed and hydrogenation characteristics. The alloys with Ca-rich and TM-rich compositions were investigated preferentially because of large unexplored regions in most of the reported ternary isothermal sections of the phase diagrams. However, most of examined alloys consisted of only already known phases, and the Ca-Cu-Al ternary alloy samples invariably disproportionated to form CaH_2 and intermetallic compound phases during hydrogenation.

Thus, neither new intermetallic compounds nor their corresponding hydrides were discovered in this Project. However, it is thought that it is very important for "MH frontiersmen" to determine phase diagrams and to use that working format to search for new phases in unexplored ternary systems.

Based on the results of this project, a new project will be planned in order to search for new intermetallic compounds and alloys that have the possibility of large hydrogen storage capacities. Sequential research will be performed to investigate phase relations in ternary system, that is (I or II group element)-(3d transition element)-(other element), where isothermal phase diagram sections have not been established. In addition, the hydrogenation characteristics of newly discovered phases will be accordingly examined.

References

[1] E. Veleckis. *J. Less-Common Met.*, **80** (1981) 241
[2] G. D. Sandrock, "*Proc. 12th Intersoc. Energy Conv. Engin. Conf."*, **1** (1977) 951
[3] A. Yoshikawa and T. Matsumoto, *J. Less-Common Met.*, **84** (1982) 263
[4] Y. K. Cho, R. Yamamoto, M. Doyama, S. Ono, K. Imanari and T. Tabata, *J. Less-Common Met.*, **88** (1982) 125
[5] G. D. Sandrock, J. J. Murray, M. L. Post and J. B. Taylor, *Mat. Res. Bull.*, **17** (1982) 887
[6] K. Yagisawa, A. Yoshikawa and T. Matsumoto, *J. Less-Common Met.*, **99** (1984) 205
[7] S. Misawa, H. Sugawara, S. Ikeishi and S. kitamura, *J. Jpn. Inst. Met.*, **46** (4) (1982) 380
[8] H. Österreicher, K. Ensslen, A. Kerlin and E. Bucher, *Mat. Res. Bull.*, **15** (1980) 275
[9] G. Petzow and G. Effenburg, "Ternary Alloys", vol. **3**, vch verlagsgesellschaft, Weinheim, Germany (1990) 618
[10] G. Petzow and G. Effenburg, *"Ternary alloys"*, Vch Verlagsgesellschaft, Weinheim, Germany, **3** (1990) 589
[11] M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, or General Electric Co., Business Growth Services, Schenectady, NY (1958)
[12] G. Petzow and G. Effenburg, *"Ternary alloys"*, Vch Verlagsgesellschaft, Weinheim, Germany, **3** (1990) 592
[13] S. R. Nagel, U. M. Gubler, C. F. Hague, J. Krieg, R. Rapka, P. Ölhafen, H. J. Güntherodt, J. Evers, A. Weiss, V. L. Moruzzi and A. R. Williams, Phys Rev. Lett., **49** (1982) 575