マイクロ XRF による水素吸蔵合金の超微量元素添加共晶ナノ微細組織形成機構の解明
Determining the role of trace element additions in the formation of eutectic nano-structures in Mg based hydrogen storage alloys using micro X-ray fluorescence

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Magnesium based hydrogen storage alloys are potentially suitable for numerous applications. This research uses micro-XRF technique at BL47XU to investigate the calcium and sodium distribution in an non-faceted/faceted hypo-eutectic Mg-14wt%Ni alloy modified by 780ppm calcium and 2400ppm Na. This will provide information critical to understanding the modification mechanism in Mg-Mg_2Ni hydrogen absorption alloys and also why these elements alter the hydrogen storage properties.

Keywords: Hydrogen absorption alloys, XRF, Eutectic, Magnesium

Introduction:

Magnesium based hydrogen storage alloys are potentially suitable for numerous applications, including integration into automotive fuel cell systems. The intermetallic compound Mg_2Ni reversibly forms Mg_2NiH_4 and can hold as much as 3.6wt% hydrogen[1], one of the highest capacities of hydrogen absorbing intermetallic compounds. Recently, thixotropic casting techniques followed by partial remelting and quenching, have been used to produce hypoeutectic Mg-Ni alloys consisting of magnesium rich dendrites surrounded by refined Mg-Mg_2Ni eutectic[2]. It is likely that the nickel or Mg_2Ni phase acts as a catalyst, improving the kinetics of hydrogen transfer into the magnesium rich solid phases. This realisation has encouraged research using nano-technology and powder metallurgy techniques. These techniques are attractive because they result in large interface areas and introducing crystallographical defects such as dislocations, which could distribute potential catalysts throughout the microstructure enabling them to have a widespread influence on the kinetics of the reaction. Unfortunately, nano-scale powder metallurgy techniques offer limited control over the crystallographic structure of the phases and would be prohibitively expensive for the mass production of commercial hydrogen-storage components. Eutectic solidification is an ideal means of not only obtaining a large interface area between two or more phases but also, with the use of 'modifying' additions it is possible to introduce a large number of crystallographical defects such as twins. Modification results in a structural transformation of faceted eutectic phases from a needle-like to a fibrous morphology. The formation of this fine fibrous eutectic occurs in Al-Si alloys with additions of elements such as strontium, calcium and sodium and has been explained using a theory of impurity-induced twinning (IIT) where impurity atoms encourage the perpetuation of a twin plane re-entrant edge (TPRE) enabling more flexible growth of the faceted Si phase. In our previous micro-XRF experiments at SPring-8 BL47XU (2006A1645), we reported that in Sr modified eutectic silicon the Sr was homogenously distributed in eutectic Si[3]. The impurity-induced twinning theory suggests that a high density of twinning occurs in the faceted phase in modified alloys because atoms of the modifier are adsorbed onto the growth steps of the faceted phase at solid-liquid interface, thus poisoning the regular TPRE growth. This research uses micro-XRF technique to investigate the calcium and sodium distribution in an non-faceted/faceted hypo-eutectic Mg-14wt%Ni alloy modified by 780ppm calcium and 2400ppm Na. This will provide information critical to understanding the modification mechanism in Mg-Mg_2Ni hydrogen absorption alloys and also why these elements alter the hydrogen storage properties.

Experimental:

The samples used in the experiments were Mg-14wt%Ni alloys modified with either 780ppm calcium or 2400ppm Na. In addition to this major component of the experiment the technique was used in two supplementary experiments. The first of these supplementary experiments was the examination of Eu and Yb impurity elemental distributions in rare earth modified Al-10wt%Si alloys and the Ge distribution in Sn-0.7wt%Cu-0.05wt%Ni. For this report, the result of Ca in Mg-14wt%Ni are described. The

micro-XRF experiment was performed at an undulator beamline 47XU of SPring-8, Japan. A schematic diagram of the experimental set-up is shown elsewhere[4, 5]. The undulator radiation was monochromatized at 6.1 and 12keV by passing through a liquid-nitrogen-cooled Si 111 double-crystal monochromator. A Fresnel zone plate was used as an X-ray focusing device to produce a fine probe. The FZP was fabricated by the electron-beam lithography technique at NTT Advanced Technology Co. Ltd. A zone structure with 1-μm-thick tantalum is deposited onto a 2-μm-thick SiC membrane. The diameter is 155 μm. The outermost zone width is 100 nm. In this setup, the beam size was 180 nm (vertical) x 150 nm (horizontal) and the total flux of the focused probe was ~4.4 x 10^9 photons/sec. The focused X-ray beam was used as the probe. The samples were mounted on a translation scanning stage with a motion accuracy of better than 30 nm. The XRF spectra were measured with a Si drift diode detector (Rontec Xflash D301). An x-ray path set between the sample and the detector was purged with helium gas in order to reduce absorption-loss by the air.

Results and Discussion:

The XRF spectra corresponding to the sample containing Ca is shown in Figure 1. A spectra is taken from a region of approximately 50x50μm incorporating magnesium dendrites, eutectic magnesium and eutectic Mg_2Ni, and clearly indicates the presence of magnesium and calcium. A micro-XRF elemental map of a Mg-14wt%Ni sample containing 780ppm Ca (scan pitch: 50 nm, signal integration time for each point: 1 sec) is shown in Figure 2 (a and b). This detection of Mg is significant as it is the first low atomic number element of Mg detected by micro-XRF in our experiments. In a previous experiment (2006A1645), we could not detect the elements lighter than Al. It is clear from the mapping results that calcium is present in the eutectic Mg_2Ni phase, and is of lower concentration in the eutectic magnesium and primary dendritic magnesium phase. From this result, trace levels of Ca addition result in not only changes to the eutectic microstructure (morphology) of eutectic Mg-Mg_2Ni, but also result in a unique 'self-distribution' of Ca atoms concentrated in the intermetallic Mg_2Ni phase. The combination of the morphological change and trace element distribution in combination with possible changes in the density of crystallographic defects and the chemical nature of the modifying addition are all likely to contribute to the unique hydrogen storage properties of modified magnesium based hydrogen storage alloys. These nano-structures are formed in-situ during solidification from the melt and it is unlikely they could be easily replicated by other nano-fabrication methods.

Future Works:

It would be interesting to determine whether other known modifier/enhancer elements in Mg-14wt%Ni alloys known to induce changes in the hydrogen storage properties, such as Na, segregate in the same manner. If so, this would lend itself to the development of a theoretical model of modification in this alloy system.

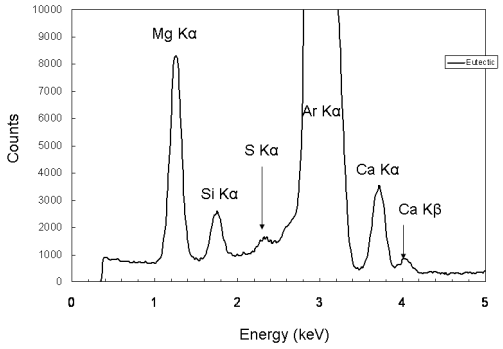

Fig. 1. XRF spectra of Ca modified Mg-Mg_2Ni sample.

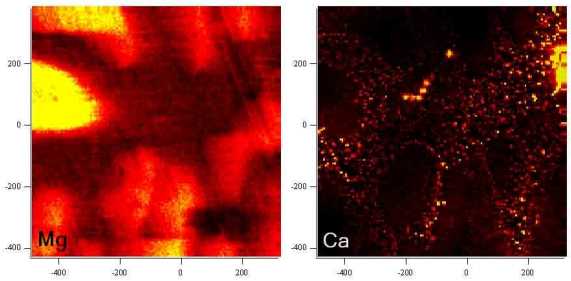

Fig. 2. μ-XRF images taken by the scan of (a) Mg and b)Ca in Mg-Mg_2Ni at the Ca addition level of 780ppm (scan pitch: 50 nm, integration time: 1 sec)

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