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Electronic structure of nanocrystalline and polycrystalline hydrogen storage materials

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Abstract

To optimise the choice of the compounds for a selected application, a better understanding of the role of each alloy constituent on the electronic properties of the material is crucial. In this work, we study experimentally the electronic properties of nanocrystalline and polycrystalline $(Mg_{1-x}M_x)_2Ni$, $(Mg_{1-x}M_x)_2Cu$, $La(Ni_{1-x}M_x)_5$, and $Ti(Ni_{1-x}M'_x)$ (M = Mn,Al; M' = Fe,Mg,Zr) alloys. The nanocrystalline and polycrystalline samples were prepared by mechanical alloying (MA) followed by annealing and arc melting method, respectively. All X-ray photoelectron spectroscopy (XPS) spectra were measured immediately after cleaning of the sample surface in a vacuum of 8×10^{-11} mbar. Furthermore, we have measured XPS spectra of *in situ* prepared nanocrystalline and polycrystalline $LaNi_5$, TiNi, and Mg_2Ni thin films and compared with those obtained for *ex situ* prepared bulk materials. The substitution of Mg in Mg_2Ni and Mg_2Cu, Ni in $LaNi_5$ and TiNi by transition metals leads to significant modifications of the shape and width of the valence band of the nanocrystalline as well as polycrystalline samples. Especially, the valence bands of the MA nanocrystalline alloys are considerably broader compared to those measured for the polycrystalline samples. Results also showed that the strong modifications of the electronic structure of the nanocrystalline alloys could significantly influence on their hydrogenation properties.

Keywords: Nanocrystalline alloys; Metal hydrides; Electronic structure; XPS

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1. Introduction

In recent years many new developments have occurred in metal hydrides, from the introduction of new, non-conventional methods of fabrication, surface treatment, or by discoveries of new hydride phases [1,2]. Hydrogen storage materials research is entered a new and exciting period with the advance of the nanocrystalline alloys, which show substantially enhanced absorption/desorption kinetics, even at room temperatures. A large number of experimental investigation on $LaNi_5$-, TiFe-, TiNi-, ZrV_2-type compounds have been performed up to now in relation to their exceptional hydrogenation properties [3]. Magnesium-based hydrogen storage alloys have been also considered to be possible candidates for electrodes in Ni–MH batteries [4].

In order to optimise the choice of the intermetallic compounds for a selected application, a better understanding of the role of each alloy constituent on the electronic properties of the material is crucial. Several semi-empirical models [5,6] have been proposed for the heat of formation and heat of solution of metal hydrides and attempts have been made to justify the maximum hydrogen absorption capacity of the metallic matrices. These models showed that the energy of the metal–hydrogen interaction depend both on geometric and electronic factors.

The chemical composition of the metal alloy is one of the most important factors in the metal–hydrogen system. The equilibrium conditions are reflected in the phase diagram, which dictates the respective phase composition under given temperature and pressure. Introducing metastable phases may result in totally different behaviour of the alloy. Mechanical alloying (MA) has been recently used, as another processing method, to make nanocrystalline metal hydride materials [7–11]. This process consists of repeated

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fracture, mixing and cold welding of a fine blend of elemental particles, resulting in size reduction and chemical reactions [12]. As nonequilibrium processing method MA can be utilised to produce large quantities of materials at relatively low cost.

On the other hand, the nanocrystalline metal hydrides offer a breakthrough in prospects for practical applications. Their excellent properties (significantly exceeding traditional hydrides) are a result of the combined engineering of many factors: alloy composition, surface properties, microstructure, grain size, and other. In the development of nanocrystalline hydrides, the goal is not only to improve operational properties of the existing hydrides, but also (more importantly) to create a new generation of materials, with the properties being designed and controlled to fulfil the particular demands of different applications.

In this paper, we study the electronic properties of polycrystalline and nanocrystalline hydrogen storage alloys using X-ray photoelectron spectroscopy (XPS). The structure of the samples has been studied by X-ray diffraction (XRD). Their bulk chemical compositions were measured using X-ray fluorescence (XRF) method. The surface chemical compositions and the cleanness of the samples were studied by XPS and Auger electron spectroscopy (AES). The subsurface chemical compositions were studied by XPS and AES using Ar^+ ion beam bombardment for removing of a surface layer.

2. Experimental procedure

The nanocrystalline TiNi-, $LaNi_5$-, Mg_2Cu-, and Mg_2Ni-type alloys were prepared using MA followed by annealing. MA was performed under an argon atmosphere using a SPEX 8000 D Mixer Mill. The round bottom stainless steel vial, which was equipped with a connection valve for evacuation or introduction of argon, was degassed for 12 h below 0.01 Pa. Then high purity argon was introduced into it, the pressure of which was up to 150 kPa. The vial was always handled in argon atmosphere to minimise uncontrolled oxidation. The composition of the starting powder mixture corresponded to the stoichiometry of the ideal reactions. In the case of $LaNi_5$-, and Mg_2Ni (Mg_2Cu)-type compounds an extra 8 wt% of lanthanum and magnesium was used, respectively. The high purity elemental powders (Mg $\leqslant 300\,\mu m$, Al $\leqslant 75\,\mu m$, Cr 1–5 μm, Mn $\leqslant 45\,\mu m$, Fe $< 10\,\mu m$, Co 2 μm, Ni 3–7 μm, Zr 149 μm, Mo $\leqslant 10\,\mu m$ and La $\leqslant 425\,\mu m$) were mixed and loaded into the vial in the glove box (Labmaster 130) containing an argon atmosphere ($O_2 \leqslant 2$ ppm and $H_2O \leqslant 1$ ppm). The as-milled powders were heat treated (see Refs. [16,20–23] for details) under high purity argon, respectively, to form ordered phases. Furthermore, we have also prepared Mg_2Ni/Pd and Mg_2Cu/Pd composites with Pd content up to 10 at%. The MA and annealed Mg_2Ni (Mg_2Cu) powder was mixed with 10 wt% Pd powder (74 μm, purity 99.9%) and milled for 1 h in a SPEX Mixer Mill. The weight ratio of hard steel balls to mixed powder was 30:1.

The powders were examined by XRD analysis, using Co–Kα radiation, at various stages during mechanical alloying, prior to annealing and after annealing. Independently, the MA process has been studied by scanning electron microscopy (SEM). The change in the structure of powdered samples was observed using atomic force microscope (AFM) (Nanoscope IIIa-Digital Instruments, USA).

Additionally, the polycrystalline TiNi- and $LaNi_5$-type alloys were prepared by induction melting stoichiometric amounts of the constituent elements (purity 99.8% or better) in a high purity argon atmosphere. The as cast ingots were sealed in quartz tubes under argon and homogenized at 1173 K for 3 days and then rapidly cooled to room temperature in water. Independently, the polycrystalline Mg_2Cu (Ni) alloy was synthesised by a diffusion method as follows. The mixed powders were pressed, sealed in quartz tubes under argon, homogenised at 1173 K for 6 h and then rapidly cooled to room temperature in water. Finally, the alloy lump was pulverised in few hydriding/dehydriding cycles to a fine powder.

Furthermore, we have also prepared polycrystalline and nanocrystalline TiNi, $LaNi_5$, and Mg_2Ni alloy thin films, as well as pure Ni, La, Ti, and Mg layers. The thin film samples were deposited onto glass substrates in the temperature range 285–700 K using computer-controlled ultra high vacuum (UHV) magnetron co-sputtering. Ni (Fe) and La (Ti, Mg) targets were sputtered using DC and RF modes, respectively. The base pressure before the deposition process was lower than 5×10^{-8} Pa. The chemical composition and the cleanness of all layers was checked *in situ*, immediately after deposition, transferring the samples to an UHV (4×10^{-9} Pa) analysis chamber equipped with XPS and AES [4]. The XPS spectra were measured with Al–K_α radiation at 1486.6 eV at room temperature using a SPECS EA 10 PLUS energy spectrometer. All emission spectra were measured immediately after *in situ* sample transfer in a vacuum of 8×10^{-9} Pa. The deposition rates of the prepared thin films are individually checked by a quartz thickness monitor. The total thickness of the samples was about 50 nm. The assumed thickness and composition of the deposited films were also revealed by XRF analysis.

The bulk chemical composition of the sample was measured under environmental conditions by XRF method using pure La (99.9 wt%), Ni (99.998 wt%), Co, (99.99 wt%) Fe (99.99 wt%), Mg (99.98 wt%), Ti (99.99 wt%), and Al (99.99 wt%) as standard materials. The surface chemical composition and the cleanness of the samples were measured in UHV using XPS, AES, and ion gun etching system.

The surface of the sample was formed to be flat and cleaned of oxides with a file. Next, the sample was washed in acetone, polished, and subsequently introduced in high vacuum chamber (10^{-4} Pa). Before loading to the UHV preparation chamber, the sample of studied material with