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Nicola Bazzanella, Riccardo Checchetto, and Antonio Miotello

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Catalytic effect of mixed Zr–Fe additives on the hydrogen desorption kinetics of MgH_2

Nicola Bazzanella,[a] Riccardo Checchetto, and Antonio Miotello
Dipartimento di Fisica, Università degli Studi di Trento, I-38050 Povo (Trento), Italy

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Mg films containing Fe–Zr mixed additives were prepared by rf sputtering and their hydrogen sorption kinetic was studied by Sievert technique. We observed that mixed Fe–Zr additives improve the H_2 desorption kinetics better than singly Fe or Zr. X-ray diffraction analysis evidences that mixed additives optimize the Fe distribution that forms smaller clusters than in Mg sample with single Fe catalyst. The presence of mixed additives, with Fe having larger diffusivity than Zr, contributes to maintain the atomic Zr dispersion in the Mg matrix, thus, favoring the presence of a greater number of nucleation sites for MgH_2 to Mg transformation. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2840180]

Despite the large number of papers published in the last years on the hydrogen sorption kinetics in Mg based materials, there is not a clear understanding of the catalysis mechanisms due to the presence of transition metal (TM) or transition metal oxides (TMOs) nanoclusters. Recent experiments seem to support the idea that, in nanocrystalline ball-milled magnesium, TM and TMO nanoclusters promote the formation of a destabilized $MgH_{2-\delta}$ phase. Because of the abundance of H vacancies in this phase, the hydrogen diffusion results accelerated: this phase, thus, acts as gateway through which hydrogen enters into the Mg grains. This substoichiometric phase is supposed to grow in presence of the TMO additive during the ball-milling process because the TMO additive destabilizes the magnesium hydride in regions close to the MgH_2-oxide interfaces by the formation of mixed Mg-TM oxides.[1] When the additive is TM, these mixed oxide regions result from mechanical alloying of the TM nanoclusters and the MgO surface layer of the Mg particles.[2]

In previous papers, by studying samples prepared by rf sputtering, we observed that the presence of TM nanoclusters dispersed in the MgH_2 matrix accelerates the H desorption kinetics[3] and there was no evidence of any oxide phase, as studied by x-ray diffraction analysis (XRD), transmission electron microscopy, and extended x-rays absorption fine structure (EXAFS) analysis.[4] We suggested that TM nanoclusters act as preferential sites for *h*-Mg (hexagonal) nucleation and promote the formation of an interconnected network of *h*-Mg domains, where H diffusion preferentially occurs.[3,4] Two additional effects were also evidenced by the experiments. First, in Mg samples with Nb content in the at. % level, the hydrogen desorption kinetics of as prepared samples, where Nb is not clusterized, was faster than that observed in the fully activated samples where Nb clusters are present.[5] Second, catalytic effects were also observed when the metallic additive was present at levels lower than 0.1 at. % in the Mg matrix,[5] that is close to the solubility limit of Nb in Mg. The previous evidences indicate that the additive can play a catalytic role also when atomically dispersed in the hydride matrix.[5] The desorption curves presented the same kinetics (nucleation and growth mechanisms) and activation energy as that of the pure MgH_2 samples but a shorter nucleation time of the *h*-Mg phase. We, thus, suggested that Nb atoms dispersed in the Mg matrix act as nucleation centers for the *h*-Mg phase in the parent MgH_2 phase.

In this paper, we present a study on the hydrogen desorption from magnesium hydride samples containing mixed metallic additives, Fe and Zr, at atomic percent level. As previously discussed, the homogeneous distribution of the catalyst in form of few atoms aggregates results more efficient in accelerating the hydrogen desorption from MgH_2 than the situation in which large clusters are formed.[5] The additive mixing studied in this paper will represent a route to limit the aggregation of one or of both additives in form of large clusters, thus, favoring a better distribution of catalysts (small clusters or a few atoms aggregates) into the whole volume of the magnesium hydride. To this purpose, we have used Zr and Fe because they have catalytic effects when dispersed in form of nanocluster in the MgH_2 matrix[6] and because they do not form binary phases with Mg matrix.[7] Finally Zr is heavier than Fe and has larger atomic diameter, 4.32 versus 3.44 Å. They, thus, have different mobility values and we, thus, expect different clustering processes when sharing the same host matrix (Mg) in the sense that mainly the faster atoms (Fe in the present case) will make use of the disposable (defects) nucleation centers.

Mg films with thickness in the $10-20\ \mu m$ range were synthesized on polished graphite (g-C) substrates by rf magnetron sputtering using high purity Ar (99.999%) as working gas. The addition of the metallic elements to the Mg samples was obtained by putting over the Mg target small Zr and Fe fragments. The additive concentration was measured after deposition by energy dispersion spectroscopy (EDS) analysis. The Mg film samples were coated with a 15 nm Pd capping layer using a Pd target (99.95% purity) without interrupting the vacuum conditions. Details on the deposition procedure are described elsewhere.[3,8] The Mg films peeled off from g-C substrate immediately after exposure to air: self-supporting film samples were then inserted in a Sievert-type apparatus[9] to study the hydrogen absorption and desorption kinetics. The activation procedure consisted on repeated absorption and desorption cycles at 623 K and 1.000 (absorption) or 0.015 (desorption) MPa H_2 gas pressure. The

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[a] Electronic mail: bazzanel@science.unitn.it.

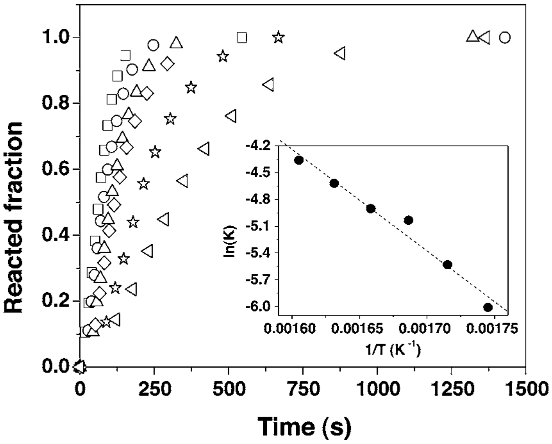

FIG. 1. Hydrogen desorbed fraction vs time at various temperatures for the Mg sample with mixed Fe–Zr additives at (□) 623 K, (○) 613 K, (△) 603 K, (◇) 593 K, (★) 583 K, and (▷) 573 K. In the inset, we present the Arrhenius plot of the desorption rate constant k. The straight line is the least square fit.

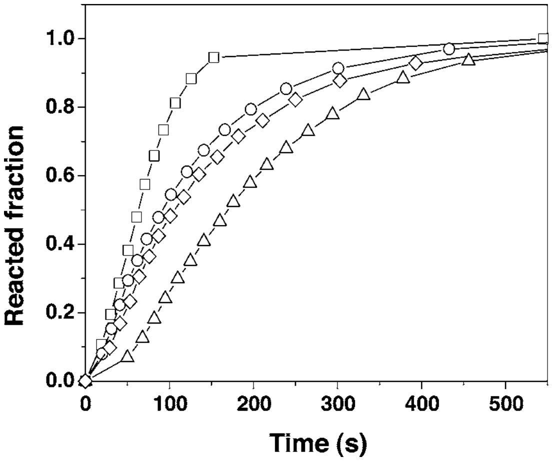

FIG. 2. Hydrogen desorbed fraction vs time at 623 K of MgH_2 sample with Zr (△), Fe (○), and Nb (◇) single additives and mixed Fe–Zr additives (□). The lines are only a guide for the eyes.

structural characterization of the samples was carried out by x-ray diffraction analysis (XRD) in conventional Bragg-Brentano configuration (θ-2θ) using the Cu Kα radiation ($\lambda = 1.5414$ Å).

SEM and XRD analysis of the as-deposited film (not reported here) showed a columnar growth of magnesium film with no evidence of metallic Fe and Zr. This means that the presence of the additive is in atomic form or in form of few atoms aggregates, as previously observed with Mg samples containing the Nb additive.[4] In the present experiment, we used samples with (i) mixed additive content of ~5 and ~2 at. % for Fe and Zr, respectively, (ii) Fe single additive 5 at. %, and (iii) Zr single additive 3 at. %. We have used additives with at. % concentration because such additive content gives rise to very fast hydrogen desorption kinetics on fully activated MgH_2 samples and a Fe content larger than that of Zr because Fe works better as catalyst.[6]

In Fig. 1, we report the H_2 desorption curves pertinent to fully activated MgH_2 samples with Fe–Zr mixed additives. The inset shows the Arrhenius plot of the desorption rate constant (k) as evaluated by curve fitting procedure using Johnson-Mehl-Avrami theory for solid state phase transitions.[10] In Table I, we report the kinetic parameters pertinent to film samples containing the mixed additives and, as reference, those pertinent to samples with a single additive and to pure MgH_2.[3] We note that, in presence of mixed additives, the hydride to metal phase transition obeys to a nucleation-and-growth mechanism while in presence of a single catalyst (Fe or Nb, with atomic concentration greater than 2 at. %) the phase transformation has diffusive character, as shown by the different values of the reaction order n and of activation energy E_a. The most important result is the fact that the mixed additives induce faster desorption kinetic, as compared to pure MgH_2 and to MgH_2 with Fe or Nb as single additive, as shown by the $\tau_{1/2}$ parameter, defined as the interval time required to transform 50% of MgH_2 to Mg. This is also shown by Fig. 2. Here, we present the H_2 desorption curves at 623 K of MgH_2 with single catalyst, curve (○) for Fe, (△) for Zr, (◇) for Nb, and curve (□) for MgH_2 with mixed additive. Table I also indicates that the hydride decomposition kinetic with mixed additives is very similar to that of the sample with 1 at. % Nb described in Ref. 5: the order of reaction is the same and the activation energy values are very similar. The much better catalytic effect of the mixed additives is related to the impressive increase of pre-exponential factor (A) of the desorption rate constant (k) growing from $\sim 10^4$ to $\sim 10^8$ s^{-1}. We remark that the improved kinetics compared to that of the sample with Fe or Zr as single additive cannot be attributed to the larger additive content because there is a saturation effect in the desorption catalysis at additive contents of ~2 at. %.[5]

TABLE I. Evaluated values of the half reaction time ($\tau_{1/2}$) at $T = 623$ K, order of reaction (n), activation energy (E_a), and preexponential factor (A) of pure MgH_2 and samples with different catalysts (Nb, Fe, and ZrFe).

Sample	$\tau_{1/2}$ (s)	n	E_a (kJ mol^{-1} H)	A (s^{-1})
Pure Mg	3250 ± 50	4	141 ± 5	$\sim 10^8$
Mg+5 at. %Nb	110 ± 10	1	51 ± 5	$\sim 10^2$
Mg+1 at. %Nb	300 ± 10	1.5	78 ± 5	$\sim 10^4$
Mg+5 at. %Fe	100 ± 10	1	51 ± 5	$\sim 10^2$
Mg+(Fe-Zr)	70 ± 10	1.5	94 ± 5	$\sim 10^8$

In Fig. 3, we present the XRD spectrum of a fully activated sample after H_2 desorption that provides information on the physical state of the Fe and Zr additives. In the spectrum, we observe reflection peaks pertinent to Mg and the (110), (200), and (211) Bragg reflections of the α-Fe phase but no XRD peak attributable to Zr nor to any Fe–Zr phase. Because Zr and Fe as single additive cannot produce the fast desorption kinetics shown in Fig. 1, we conclude that the improved catalytic effect of the mixed additives has two causes: (i) aggregation of Fe into nanoclusters and (ii) atomic dispersion of Zr (that could also form aggregates but consisting of few atoms). We remark that the second effect has permanent character because, contrary to the samples with single additive, no evidence of Zr clustering is observed also after repeated H_2 sorption cycles.

The size of the α-Fe crystallites is determined to be lower than 20 nm by employing the Williamson–Hall method[11] according to the broadening of the (110), (200), and (211) Bragg reflection peaks in Fig. 3. We can also evaluate a low microstrain value of $\varepsilon \sim 6 \times 10^{-4}$ not observed in the Mg sample with single Fe additive. The intensity ratio

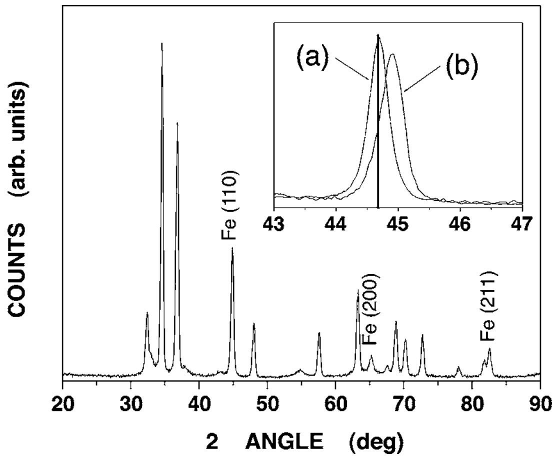

FIG. 3. XRD spectra pertinent to Mg samples with mixed Fe–Zr additives (completely activated) after H_2 desorption. In the figure, only the Fe reflection peaks are labeled and all others peaks are pertinent to *h*-Mg reflections. In the inset we present the Fe (110) reflection peak pertinent to a sample with only the Fe additive, line (a), and to a sample with mixed Fe–Zr additives, line (b). The thick line is the reference position of the Fe (110) peak (Ref. 12).

of these diffraction peaks indicates that the α-Fe nanoclusters have a random distribution in the Mg matrix. The α-Fe clusters size is lower than in Mg samples with single Fe additive, ~30 nm, as evaluated by the Bragg–Brentano analysis of the (110) reflection peak presented in the inset of Fig. 3, line (a) (this is the only α-Fe reflection in the XRD spectrum). Both samples have the same Fe content, ~5 at. % and, assuming that all Fe atoms form precipitates, we conclude that the sample with mixed additives presents a higher Fe cluster density.

The difference in the Fe clustering can be explained by the lower mobility of Zr atoms, as compared to that of the Fe atoms. Because the maximum solubility of Zr in Mg is lower than the present concentration, then Zr atoms segregate in extended defects such as grain boundaries or dislocations. In the Mg sample with Zr as single additive, after segregation upon diffusion, Zr atoms aggregate forming clusters.[6] In the sample with mixed additives, these Zr clusters are not observed. As shown by Fig. 3, the larger Fe mobility suggests that a possible mechanism impeding the Zr aggregation is the Fe clustering in the disposable nucleation centers which anticipates the Zr precipitation. The lower size of the Fe clusters in the Mg sample with mixed additives is, thus, consequence of a larger density of available nucleation sites as compared to that in the Mg sample with single Fe additive. Indeed, Zr atoms also may constitute precipitation centers for Fe atoms.

On the basis of the previously discussed Fe clustering process, we suggest that the presence of mixed additives gives rise to the optimization of the Fe cluster distribution in terms of an increased Fe nanocluster density. Because Fe nanoclusters act as nucleation centers for the *h*-Mg phase in the hydride to metal phase transition, the hydrogen desorption kinetics results, thus, accelerated.[3–6] In addition, we may also suggest that in the present samples, the Zr atoms also can act as stable and distributed active centers for *h*-Mg nucleation in the β-MgH_2 matrix during desorption, as observed in MgH_2 samples with Nb additive atomically dispersed.[5] Finally, the very high value of the preexponential factor (A) which contributes to increase the desorption kinetics should be explained.

Preliminary results showed that by lowering the Fe concentration while increasing the Zr one, then the kinetics of the hydrogen desorption tends to decrease. This proves that there is an optimum Fe and Zr atomic concentration which establishes the best kinetics conditions for cluster-assisted hydrogen desorption.

To gain a better understanding of the chemical state of the Zr additive and, thus, of the catalytic process in the mixed additive samples, we plan to carry out EXAFS analysis to analyze the atomic environment of the Zr atoms.

In conclusion, we proved that mixed additive may constitute a new route to improve hydrogen kinetics in magnesium hydrides by increasing the uniform distribution of nucleation sites for the growing of the *h*-Mg phase during hydrogen desorption.

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