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Hydrogen generation by oxidation of “mechanical alloys” of magnesium with iron and copper in aqueous salt solutions

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ABSTRACT

Oxidation processes of magnesium and magnesium “mechanical alloys” with iron and copper (1–15 wt%) in presence of aqueous solutions of sodium, cobalt, nickel and copper chlorides have been investigated. The rate of hydrogen generation increases with the increase of the transition metal content in the “alloys” and levels out for the Mg–Cu system. The overall hydrogen yield does not exceed 92% of theoretical one at the initial solution concentrations of 0.032 M and chloride/Mg molar ratios of 0.0075 (0.85 M and 0.20 for NaCl), but becomes close to 100% at double concentration of the transition metal salt solutions. The electrochemical corrosion mechanism of the magnesium oxidation process has been suggested.

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Introduction

The fundamental problem in hydrogen-based energy technologies is the development of efficient methods for hydrogen generation for later utilization in stationary and mobile fuel cells. One of the approaches actively investigated in the past several years was aqueous oxidation of light non-transition metals. Researches on this topic are mainly focused on the use of aluminum [1–4]; meanwhile magnesium is of particular interest, too, due to its substantially higher reactivity attributed to the less dense protective surface oxide than the aluminum one. Besides, MgO can be converted to a slightly soluble hydroxide in presence of moisture [5,6]. Hydrogen

yield in magnesium oxidation by water reaches 0.92 L of H₂/g that should be sufficient for small fuel cells.

The solid hydroxide layer that forms on metal surface and greatly slows the oxidation process remains a common issue to overcome when using light metals as sources of hydrogen. There are several different methods to resolve this hindrance and activate metal surface. Among those are running reactions at increased temperature, introducing of certain metal-activators, or applying mechanical methods of activation (mechanochemistry). So far, the best results were observed for magnesium alloys with Fe, Ni, Co or Cu [7–12]. Comprehensive investigations of the corrosion behavior of magnesium alloys evidenced the electrochemical mechanism

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of the process related to formation of micro-galvanic cells between Mg and transition metals [11–14].

The last decade the effect of mechanical treatment on magnesium-based materials performance in hydrolysis reactions is intensively studied. As it was demonstrated in Refs. [15,16], upon mechanical activation in ball mill it is not only mixes of magnesium with nickel that got activated, but even pure magnesium becomes oxidizable in NaCl solution. It is noteworthy that such treatment also improves rate of oxidation and overall hydrogen yield. The same tendency was confirmed for a wide range of magnesium containing alloys and mixtures subjected to high-energy ball milling in various aqueous solutions [17–22]. The authors attributed the observed phenomena to extended active surface of the milled materials, their highly defected crystal structure, and homogeneous dispersion of metal activators into magnesium matrix. The influence of the composition of reaction solutions is still under discussion. It is well known that the use of chlorides is the most efficient, since Cl^- easily destroys the hydroxide passive layer due to formation of soluble complexes. The role of cations is not quite clear. MgCl_2 and CaCl_2 solutions hindered hydrogen generation compared to NaCl [20], while the presence of transition metal halides greatly promotes the magnesium oxidation [5].

The purpose of this work was to evaluate and compare previously suggested activation methods for magnesium and “mechanical alloys” of magnesium with iron or copper for oxidation in aqueous solutions of Na, Co, Ni or Cu chlorides.

Experimental

Reagents and methods

Metals

Mg powder MPF – (GOST 6001-79); at least 99.5% pure and a specific surface area of $S = 0.2 \text{ m}^2/\text{g}$; Cu powder (GOST 1960-19) at least 99.5% pure; carbonyl iron, at least 99.8% pure.

Salts

NaCl, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, at least analytic grade.

X-ray studies were executed on the Thermo ARL X/TRA diffractometer with $\text{CuK}\alpha$ -radiation.

Mechanical treatment of Mg and “mechanical alloy” formation

Mg and its mixes with Cu or Fe at 1, 4, 7, 10 and 15 wt% were processed in planetary ball mill (AGO-2U type) with drum rotation speed of 2220 rpm for 3 min. This is an equivalent of approximately 0.2 kJ/g deformation dose as defined according to Ref. [23]. Weighting (~3 g) and mixing of initial metal powders was done under argon in M. BRAUN airtight box with residual oxygen and water content of less than 1 ppm. Mixes were then placed in 150 mL caprolon-covered steel vials containing 6 mm corundum milling balls (~66 g) and sealed. Activated samples were removed under the same conditions in the airtight box, weighted and sealed in the ampoules until the experiment. Mg loss during milling was estimated not to exceed 2%.

Released hydrogen yield assessment

To quantify the hydrogen volume released from Mg or Mg “mechanical alloys” oxidation, a standard volumetric method was used [5]. Hydrogen volume was measured at room temperature by gas burette with 2% precision. About 0.1 g of starting material was placed in a flask with 1 mL of respective salt (NaCl , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) solution. Salt concentrations were of 0.85 M for NaCl and either 0.032 or 0.064 M for all other salts. These concentrations were identified in previous studies [21,25] where hydrogen yields and reaction rates as a function of salt solution concentration and a nature of oxidized metal were investigated.

Results and discussion

Table 1 summarizes the results of X-ray analysis of mechanically activated samples and derived parameters, calculated according to [24] such as crystallite size and microstrain concentration.

Table 1 – Crystallite size, microstrain concentration and unit cell parameters for initial (Mg init.), mechanically processed (Mg mill.) magnesium, and “mechanical alloys” of Mg + n%Fe and Mg + n%Cu (n = 1, 4, 7, 10 and 15 wt%).

No	Sample composition	Average crystallite size, nm	Microstrain concentration	Crystal structure parameters for Mg and “mechanical alloys”		
				a, nm	c, nm	$V \cdot 10^2, \text{nm}^3$
1	Mg init.	52 ± 6	$1.2 \cdot 10^{-3}$	0.3211 (3)	0.5215 (8)	4.6566 (9)
2	Mg mill.	36 ± 4	$2.3 \cdot 10^{-3}$	0.3213 (5)	0.5216 (1)	4.6630 (2)
3	Mg + 1%Fe	38 ± 2	$2.2 \cdot 10^{-3}$	0.3213 (7)	0.5218 (1)	4.6650 (2)
4	Mg + 4%Fe	39 ± 2	$2.4 \cdot 10^{-3}$	0.3214 (7)	0.5219 (1)	4.6670 (2)
5	Mg + 7%Fe	40 ± 2	$2.2 \cdot 10^{-3}$	0.3215 (9)	0.5217 (2)	4.6700 (3)
6	Mg + 10%Fe	40 ± 4	$2.3 \cdot 10^{-3}$	0.3214 (2)	0.5220 (4)	4.6700 (6)
7	Mg + 15%Fe	41 ± 2	$2.6 \cdot 10^{-3}$	0.3212 (7)	0.5222 (3)	4.6670 (5)
8	Mg + 1%Cu	41 ± 3	$2.2 \cdot 10^{-3}$	0.3214 (7)	0.5220 (2)	4.6700 (2)
9	Mg + 4%Cu	39 ± 4	$2.6 \cdot 10^{-3}$	0.3212 (7)	0.5216 (2)	4.6600 (2)
10	Mg + 7%Cu	39 ± 2	$2.7 \cdot 10^{-3}$	0.3213 (7)	0.5217 (1)	4.6630 (2)
11	Mg + 10%Cu	38 ± 4	$2.3 \cdot 10^{-3}$	0.3214 (7)	0.5219 (1)	4.6690 (2)
12	Mg + 15%Cu	38 ± 2	$2.6 \cdot 10^{-3}$	0.3213 (5)	0.5216 (1)	4.6630 (1)

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