

**BALL-MILLED HYDROGEN STORAGE IN Mg-Cu – BASED ALLOYS MODIFIED BY KCl:
DISTRIBUTION OF COMPONENTS**^{1,2}Jiri CERMAK, ¹Lubomir KRAL, ^{1,3}Pavla ROUPCOVA¹ IPM AS CR, Brno, Czech Republic, EU, cermak@ipm.cz, lkral@ipm.cz, roupcova@ipm.cz,² CEITEC-IPM, Brno, Czech Republic, EU, cermak@ipm.cz³CEITEC-BUT, Brno, Czech Republic, EU, pavla.roupcova@ceitec.vutbr.cz<https://doi.org/10.37904/metal.2021.4213>**Abstract**

Magnesium and its alloys is a class of materials, which is still one of the most prospective hydrogen storage (HS) compositions. This is due before all to their high hydrogen sorption capacity and low cost. However, pure Mg must be alloyed with other elements to suppress the tendency to Mg oxidation and to improve the otherwise lazy ab/desorption kinetics and to decrease the operation temperature. Also some modifiers, as e.g., rare earth elements and alkali metals, are known to enhance the HS characteristics. It is known that sorption performance can be further substantially enhanced by nanosizing. This paper is devoted to study of distribution of components in Mg-xCu alloys (x = 9.94 – 21.56 wt%) prepared by high-energy ball-milling (BM). Elements K and Cl – as modifiers – were introduced by BM of the Mg-Cu base with addition of KCl. It was found that KCl decomposed partly into elements, which entered grains of milled blend. Chlorine anions entered preferentially the Mg-rich regions.

Keywords: Ball-milling, magnesium, copper, hydrogen storage**1. INTRODUCTION**

Nowadays, all human activities bring growing demands on storage of energy and its easy transportation. It is known for a long time that one of safe and clean energy carrier may be hydrogen [1]. Contrary to many unsolved technologic problems in the complete chain of practical hydrogen energy utilization, hydrogen is still considered for a prospective energy carrier. It is due to the important fact that hydrogen-based energetic avoids generation of greenhouse gases. Among the most challenging tasks is suitable *hydrogen* storage, which would increase the volumetric energy density. It should be remarked at this place that hydrogen compression and liquefaction is neither safe nor sufficiently effective. Hydrogen storage in the form of solid hydrides is generally considered much more prospective [2].

Under various materials, magnesium based hydrides still belong to the most promising storage ones [3]. There are, however, problems that impede the introduction of pure Mg as a storage material into the practice. The most serious ones are bias to Mg oxidation, high operation temperature of magnesium charging/discharging and lazy desorption kinetics. They originate mostly in high thermodynamic stability of the magnesium hydride MgH₂. On the other hand, abundance of Mg on the Earth, its low cost and high hydrogen storage capacity (theoretically 7.6 wt%), are advantageous features that overbalance the drawbacks.

Many attempts were undertaken to influence magnesium hydride formation enthalpy with the aim to reduce its stability and to facilitate the hydrogen desorption. Nanosizing, modifying with additives and catalysis of the sorption process are the main ways how to achieve improving in storage performance of Mg-based alloys [4].

Copper is a transition metal that was – as an additive to Mg – frequently studied. A special attention focused to structure, nanosizing and sorption catalysis of Mg storage alloys with Cu was paid, e.g., in papers [5]. Catalytic role of Cu in hydrogen sorption in Mg-Cu binary alloy system was investigated in papers [6].

Results on sorption behavior in the Mg-Cu system published up to now are still incomplete. Moreover, it was reported that small additions of halide elements, either in the crystalline form or in the dissociated form of separated ions show a significant catalytic effect upon hydrogen desorption [7]. This is why the system deserves more detailed study. As a first step, it is important to clear the modus of additive distribution. Therefore, the goal of the present paper is to investigate how the additive elements are distributed over the main phases in BM blend. As model elements, potassium and chlorine were chosen that showed beneficial effect upon the storage behavior in our recent study [8].

2. EXPERIMENTAL

Samples were prepared from pure Mg (purity 3N5) and Cu (6N) in the form of splinters. Crystalline KCl (3N) was introduced to each milling batch as an anti-sticking additive and also as a component that improves the hydrogen storage performance. It was reported [7] that halides, either in the crystalline form or in the dissociated form of separated ions show a significant catalytic effect upon hydrogen desorption.

Three experimental alloys were prepared by high energy BM in hydrogen atmosphere (under the pressure of about 1 bar) using Fritsch Pulverisette6 ball-mill. Details of sample preparation were described elsewhere [7]. Chemical composition of samples is listed in **Table 1**.

Table 1 Chemical composition (wt%)

element	composition of BM samples (wt%)		
	1	2	3
Mg	56.47	51.27	39.5
Cu	9.94	15.14	21.56
KCl	33.59	33.59	38.94

After the BM, the samples were thermally treated (activated) in order to approach the stable structure and composition. The treatment involved several sorption cycles at temperature 360 °C consisting of hydrogen charging under pressure of 50 bars for about 3 h and total hydrogen discharging. All manipulations of the milled blend were done in the glove box in a protective Ar atmosphere.

Local chemical composition was done using SEM TESCAN LYRA3 equipped with X-max80 EDS in points and/or within small rectangular areas in chosen locations at surface of each sample. For the phase analysis XRD EMPYREAN device using CoKa was used.

3. RESULTS AND DISCUSSION

Experimental results were obtained for all three samples, but the procedure and sample characterization is illustrated below for the sample 2 only, because chemical composition of the sample 2 is approximately in the centre of the concentration interval and its characteristics can be considered as exemplary for all samples. In other cases, the procedure was analogous. In **Figure 1**, typical morphology of BM powder is shown. It is illustrated that the grain size of majority particles lay between about 1 to 3 µm. Contrary to the fact that KCl acted as *anti-sticking* ingredient, the smallest particles were loosely aggregated to greater groups, which size was about 10 µm.

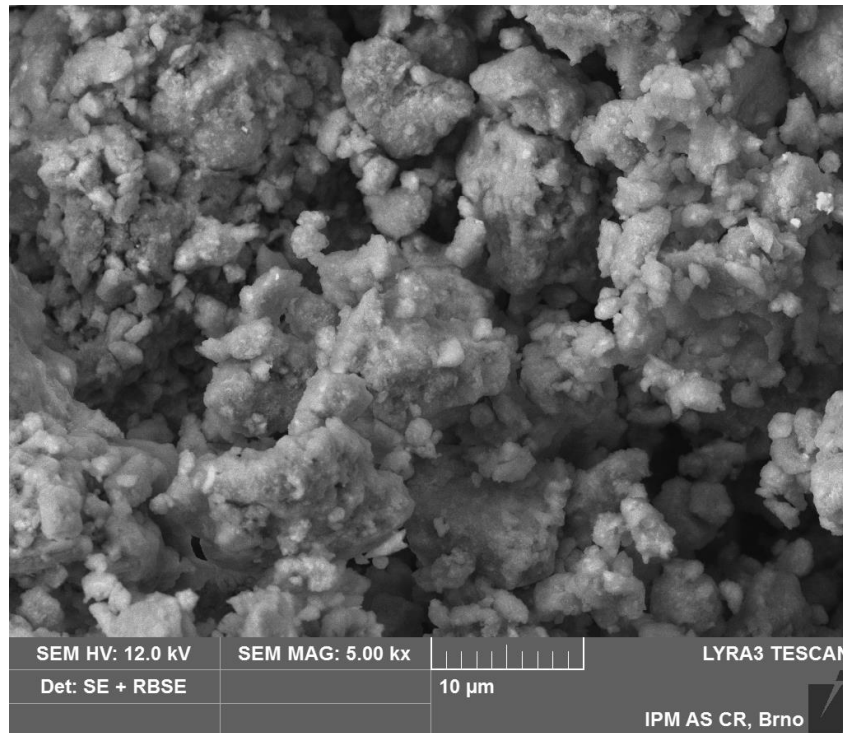


Figure 1 SEM microstructure of BM powder – example: Sample 2

The phase analysis revealed six phases in stabilized samples. Typical XRD pattern is shown in **Figure 2**.

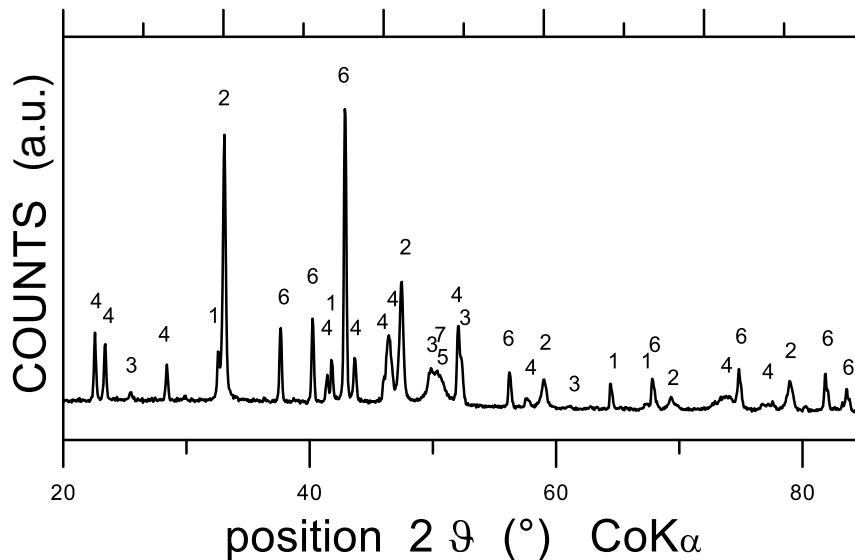


Figure 2 Typical XRD pattern obtained for activated samples: 1 – MgH_2 , 2 – KCl , 3 – $MgCu_2$, 4 – Mg_2Cu , 5 – Cu , 6 – Mg , 7 – MgO

The powder samples were glued to carbon foil and several EDS analyses were done at chosen locations at each sample – see an example in **Figure 3**.

At individual chosen point, EDS analysis was done – for the spectrum at point 3, see **Figure 4** – and the chemical composition was evaluated. Very small concentration of oxygen was present in the form of a low amount of MgO (see in **Figure 2**), which was neglected in further evaluation. Results obtained at all points are listed in **Table 2**.

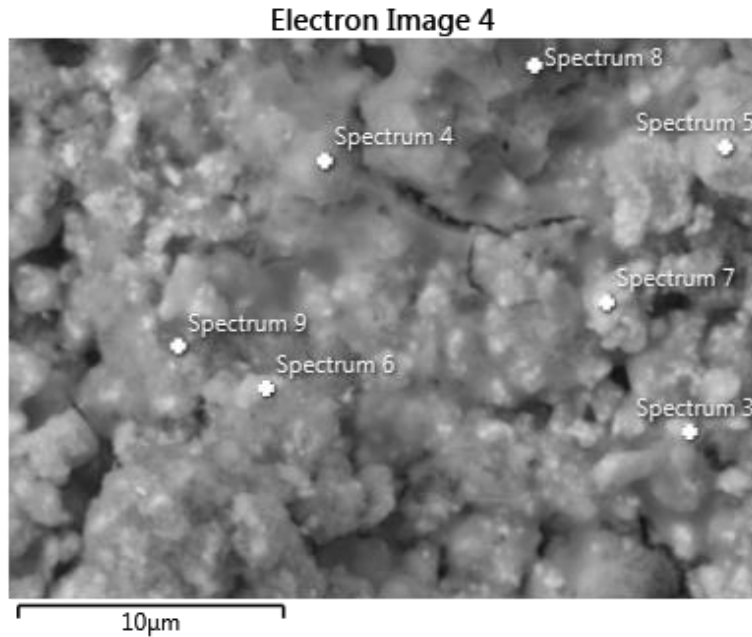


Figure 3 SEM micrograph of BM powder – example: Choice of analysed locations on Sample 2

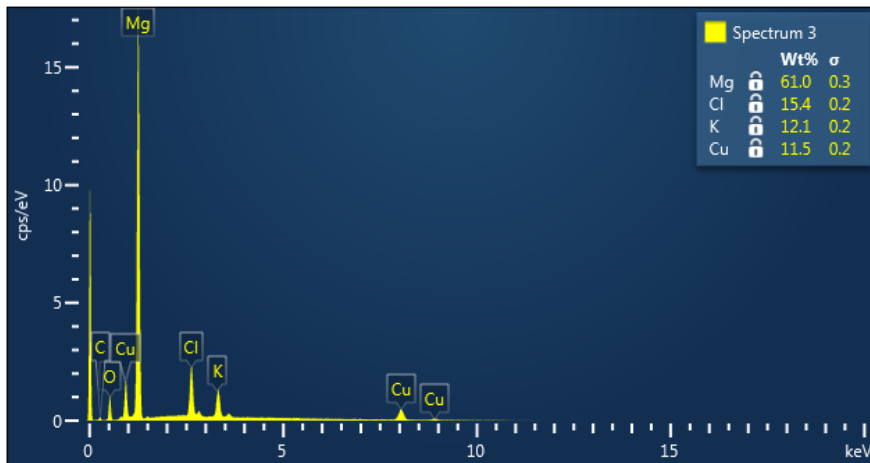


Figure 4 EDS spectrum. Example: Spectrum taken at point 3 on Sample 2

Table 2 Local chemical composition in wt% measured in points chosen at surface of Sample 2 – see **Figure 3**. Values for spectrum 1 represent the average concentration over entire area.

Spectrum Label	Spectrum 1	Spectrum 3	Spectrum 4	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8	Spectrum 9
Mg	51.27	60.99	66.46	31.25	46.38	47.56	37.55	63.71
Cl	15.34	15.41	7.41	22.49	14.09	18.12	34.52	11.84
K	18.25	12.11	9.66	37.77	16.07	20.40	24.58	6.92
Cu	15.14	11.49	16.48	8.50	23.45	13.91	3.36	17.53
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Procedure described above was repeated for all loci and for all three samples. In each location, the ratios of concentrations of Mg and Cu and concentrations of Cl and K (in atomic %) were calculated. The former ratio expresses the dominant character of the loci, the latter one scales semiquantitatively the grade of

(micro)alloying in the respective locus with K or by Cl. Results, plotted in **Figure 5** as dependence of $c_{\text{Cl}}/c_{\text{Cl}}$ vs. $c_{\text{Mg}}/c_{\text{Cu}}$, show the preference of ions and Cl to enter grains of different base composition.

It is obvious that there is a tendency to a slight enrichment of Mg-rich grains on chlorine from partly decomposed KCl. This can be easily rationalized by values of formation enthalpies of solid crystals, ΔH_f , of KCl (-435.9 kJ/mol), CuCl_2 (-218.9 kJ/mol) and MgCl_2 (-641.8 kJ/mol or $-(644.28 \pm 0.69)$ kJ/mol [9,10]). Comparing these values of ΔH_f , it can be easily concluded that KCl slightly tends to a partial decomposition and chlorine anions enter preferentially Mg-rich regions where they are solved or participate in nucleation of MgCl_2 clusters.

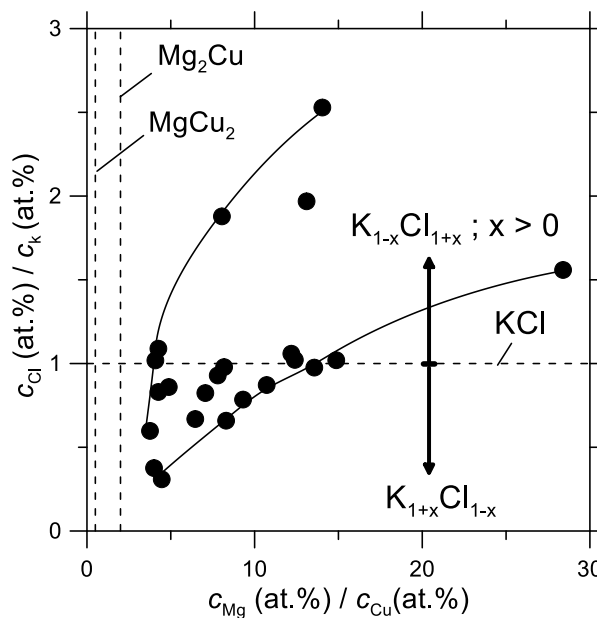


Figure 5 Local chemical composition in randomly chosen loci

4. CONCLUSION

The aim of the present paper was to investigate the composition of ball-milled and stabilized Mg-Cu(-KCl) alloys that are prospective for hydrogen storage. Special attention was paid to the stability of pristine KCl and to preference of its dissociation products, K and Cl, to grains of different chemical composition. It was found that ball-milled and stabilized alloys led to a partial decomposition of KCl and that Cl anions preferred incorporation into Mg-rich grains and K cations enter the Cu-rich component. Since the hydrogen storage in Mg-based alloys is mostly controlled by magnesium hydrides, it can be presumed that K^+ rather than chlorine anions would control their sorption performance.

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