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Hydrogen sorption characteristics of manesium-based composites with addition of $Mg_2Ni_{0.7}Co_{0.3}$ and graphite

Research Article

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Abstract: Magnesium-based composites of 75 wt% Mg - (10, 15, 20) wt% Mg2Ni0.7Co0.3 - (15, 10, 5) wt% C mechanically activated for 30 min under argon in a planetary mill, were obtained. Their absorption- desorption characteristics were investigated under a pressure P = 1 MPa and temperatures of 623, 573, 473, 423 and 373 K. Desorption was carried out at 623 K and 573 K and a pressure of 0.15 MPa. All the three composites showed improved hydriding kinetics as compared to pure magnesium. However, the desorption temperature was somewhat higher than needed for practical application.

Keywords: *Hydrogen storage material • Composite materials • Mechanical alloying • Gas-solid reaction*

1.Introduction

Magnesium, with its high absorption capacity (7.6 wt%), is a promising hydrogen storage material. The difficult activation, slow hydriding kinetics and high temperatures of absorption and desorption are a hindrance to its practical application [1]. Intense investigations on magnesium- based materials were carried out with a view to improving their absorption/ desorption characteristics by applying the high energy ball milling method and by using different types of additives.

The Mg_2Ni alloy has improved hydriding/dehydriding kinetics with respect to pure magnesium and the processes of absorption/desorption occur at lower temperatures and pressures, which are, nevertheless, too high for practical application. The ternary hydride Mg_2NiH_4 is less stable than MgH_2, but its theoretical absorption capacity is twofold lower than that of Mg (3.6 wt% H_2). This alloy can be used as an independent material for hydrogen storage or as part of magnesium composites [2-12]. Some previous investigations, carried out by the same authors had shown that additives of the type of $Mg_2Ni_{1-x}M_x$ (M=Fe or Co), improved considerably the kinetics of hydriding/ dehydriding of magnesium and a high absorption capacity was attained [13,14].

Recently many carbon containing additives such as graphite, graphene, fulerene *etc.*, [15-30] were used for improving the sorption properties of magnesium. In some studies it has been established that graphite improves the sorption characteristics of the composite due to the difficult back diffusion of oxygen to the sample surface, which is a hindrance to the restoration of the oxide layer [17,25,26]. Graphite plays the role of an antisticking agent during the grinding, thus contributing to the increase in the hydrogen-accessible surface [20]. On the other hand, during prolonged mechanical activation it may block part of the surface, thus deteriorating the hydriding kinetics. The effect of graphite on the hydriding/ dehydriding kinetics is complex and not yet clarified. It depends on the conditions of mechanical activation, on the type of the graphite used and its amount. In some cases, regardless of the restricted solubility of carbon in magnesium, after prolonged grinding in high-energy mills, phases of the type $MgNiC_x$, having negative effect on the sorption characteristics are obtained.

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An assumption of our previous work [24], suggestthat graphite plays the role of an antisticking agent, also preventing the formation of an oxide layer on the surface. The previous study composite Mg-Mg_2Ni-graphite reached a high absorption capacity and showed very good kinetic characteristics at lower temperatures. The obtained results indicated that the presence of a carbon-containing additive led to improvement of the hydrogen storage properties of magnesium. The aim of the current work is to investigate the effects of the presence and quantity of the additives $Mg_2Ni_{0.7}Co_{0.3}$ and graphite on the hydrogen sorption characteristics of magnesium.

2. Experimental Procedure

Powdery magnesium and graphite of 99.9% purity were used for the preparation of the composites 75 wt% Mg – (10, 15, 20) wt% $Mg_2Ni_{0.7}Co_{0.3}$ – (15, 10, 5) wt% C. The intermetallic $Mg_2Ni_{0.7}Co_{0.3}$ was synthesized from powdery magnesium- (99%), nickel and cobalt of 99.9% purity. Pellets of a mixture corresponding to the composition $Mg_2Ni_{0.7}Co_{0.3}$ were heated in an argon atmosphere at 823 K for 120 h. The composites Mg - $Mg_2Ni_{0.7}Co_{0.3}$ - C were obtained by mechanical grinding in a Pulverisette 6 Fritsch planetary ball mill under argon for 30 min using stainless steel balls, the ball to sample weight ratio being 10:1, and the rotation speed, 200 rpm. The purity of argon and hydrogen was 99.998% and 99.999% respectively, delivered by Messer. The ball milled samples were placed in a stainless steel gas-solid reactor. The hydrogen absorption- desorption characteristics of the composites were determined by isothermal measurement of sorption from the pressure change by dosing between calibrated volumes, also known as volumetric or Sievert's method described in [27]. Hydrogen absorption proceeded at temperatures of 623, 573, 473, 423, 373 K and a pressure P = 1 MPa. The desorption was carried out at 573 and 623 K and P = 0.15 MPa. The phase composition of the ball milled, hydrided and dehydrided composites was controlled by X-ray phase analysis (Bruker D8 Advance diffractometer with Cu-Kα radiation and SolX detector).

Additional characterization of the samples was made by SEM (JSM–5510 JEOL), and BET specific surface area measurements. The transfer from the ball milling vial to the device for measuring the absorption/desorption properties, X-ray diffraction, SEM and BET analyses of the samples was carried out in air.

3. Results and discussion

X-ray phase analysis of the initial composites (Fig. 1) shows the presence of the main components. There is some difference in the intensity of the diffraction patterns of C and the Mg_2Ni-type phase, which can be explained by the variation of the composition. It is also visible that the augmentation of the quantity of graphite does not change the level of the crystallinity. The X-ray phase analysis of the hydrided samples (Fig. 2) indicates the presence of MgH_2, Mg_2NiH_4, C and a small amount of unreacted Mg and MgO. The latter has probably been formed during the interaction of the unreacted Mg with the oxygen present, although in small amounts, in hydrogen as well as the oxygen from the air after opening the reactor where hydriding takes place. It should also be taken into account that the initial magnesium is also covered by a layer of MgO which is destructed during the hydriding but it may, after that, be restored.

Fig. 3 shows SEM microphotographs of the mechanically activated composites with 5, 10 and 15 wt% carbon (a,b,c) as well as those of the hydrided samples (d,e,f). The particles are with irregular shape and with different size. A lot of small particles with a size of several µm are bonded in agglomerates with size 30-50 µm. A decrease in particle size is evident with the increase in carbon content. Ruggeri *et al.* [20] concluded that carbon addition does not affect the morphology of the MgNi alloy prepared by mechanical alloying. Even in small proportion (1 wt%) it was shown by the same authors that graphite minimize the welding of the particles. If we consider that the graphite addition inhibits the welding between small particles during ball milling into agglomerates, it should play the role of an anti-sticking agent. On the other hand to prove with certainty this role of graphite, one has to investigate the morphology of the composite during prolonged ball milling. After hydriding of the composites, finer particles and cracks are formed.

The BET specific surface areas of the composites

Table 1. Specific surface area of the investigated composites

Composite	Specific surface area $m^2 g^{-1}$
75% Mg – 20% $Mg_2Ni_{0.7}Co_{0.3}$ – 5% C - ball milled	3
75% Mg – 20% $Mg_2Ni_{0.7}Co_{0.3}$ – 5% C – hydrided	12
75% Mg – 15% $Mg_2Ni_{0.7}Co_{0.3}$ – 10% C - ball milled	3.1
75% Mg – 15% $Mg_2Ni_{0.7}Co_{0.3}$ – 10% C – hydrided	20.6
75% Mg – 10% $Mg_2Ni_{0.7}Co_{0.3}$ – 15% C - ball milled	3.7
75% Mg – 10% $Mg_2Ni_{0.7}Co_{0.3}$ – 15% C - hydrided	28.7

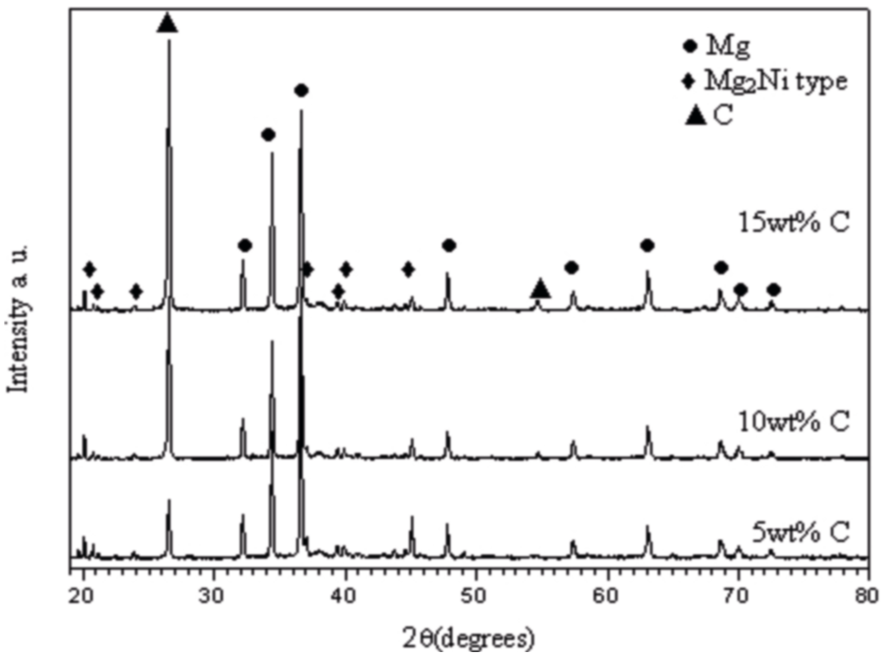


Figure 1. X-ray patterns of the composites 75% Mg – (10, 15, 20)% $Mg_2Ni_{0.7}Co_{0.3}$ – (15, 10, 5)% C as- prepared

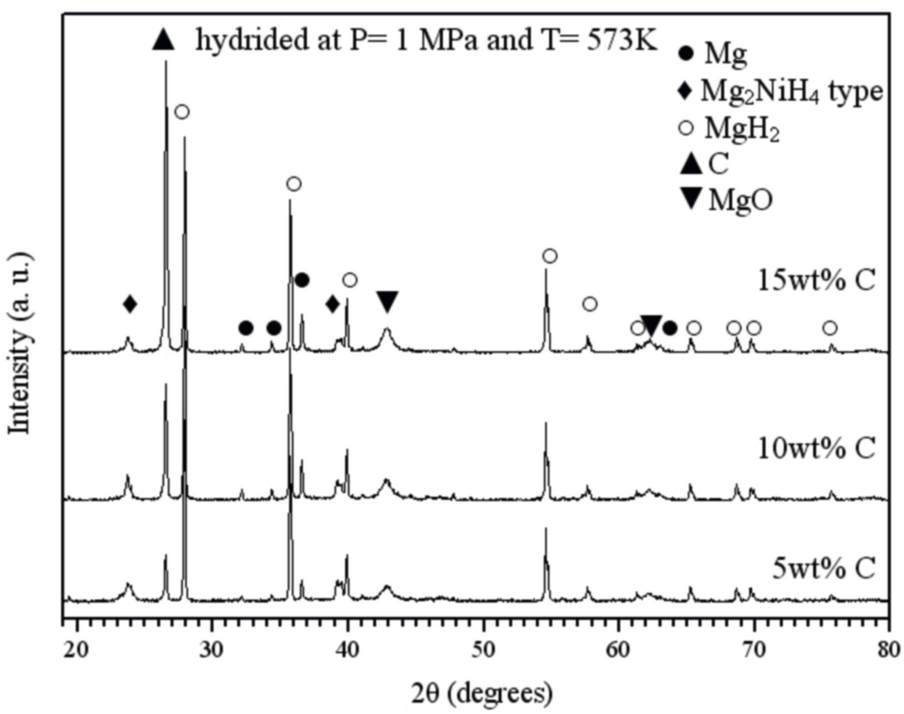
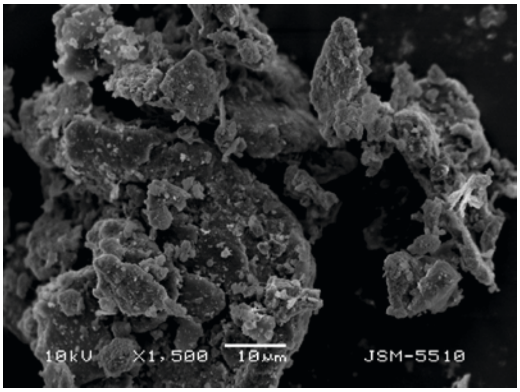
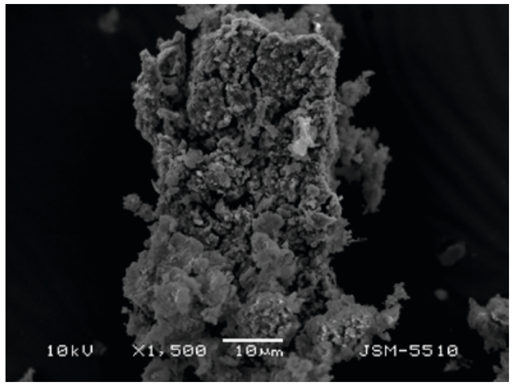


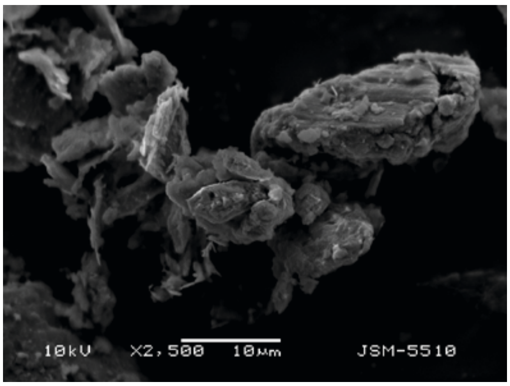
Figure 2. X-ray patterns of the composites 75% Mg – (10, 15, 20)% $Mg_2Ni_{0.7}Co_{0.3}$ – (15, 10, 5)% C after hydriding



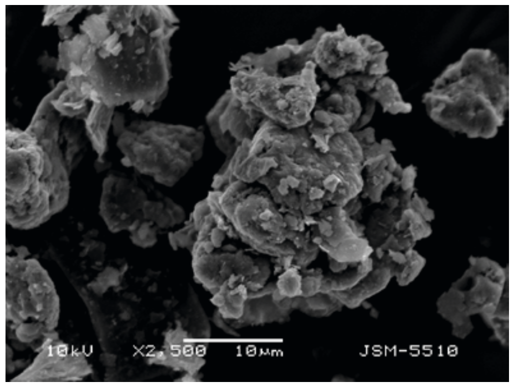
75 wt% Mg - 20 wt% Mg2Ni0.7Co0.3 - 5 wt% C
a)



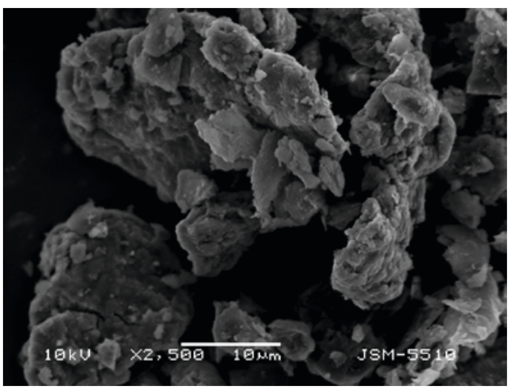
d)



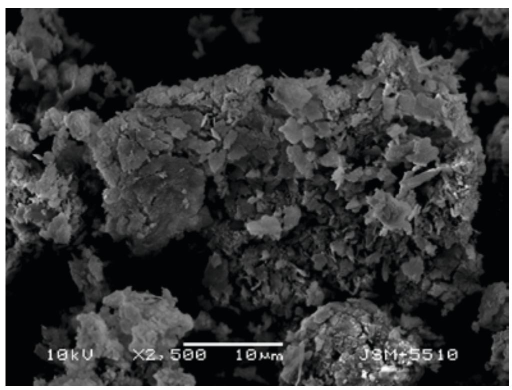
75 wt% g -15 wt% Mg2Ni0.7Co0.3 -10 wt% C
b)



e)



75 wt% g -10 wt% Mg2Ni0.7Co0.3 -15 wt% C
c)



f)

Figure 3. SEM microphotographs of the powdery composites:75% Mg – 20% $Mg_2Ni_{0.7}Co_{0.3}$ –5% C a) mechanoactivated; d) hydride 75% g – 15% $Mg_2Ni_{0.7}Co_{0.3}$ – 10% C; b) mechanoactivated; e) hydrided 75% g – 10% $Mg_2Ni_{0.7}Co_{0.3}$ – 15% C; c) mechanoactivated; f) hydrided

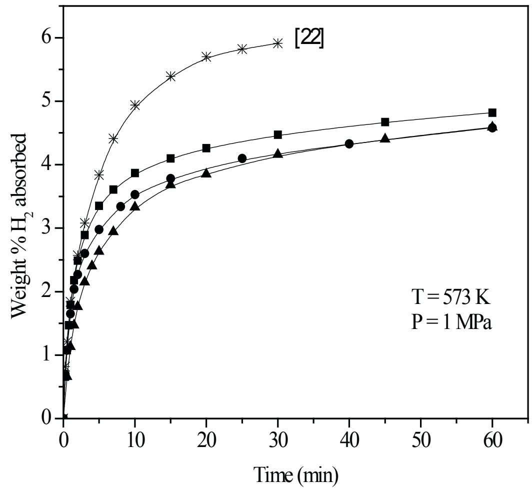


Figure 4. Kinetic curves of hydriding at 573 K and P = 1 MPa of the composites:
■ - 75% g -20% $Mg_2Ni_{0.7}Co_{0.3}$-5% C;
● - 75% g -15% $Mg_2Ni_{0.7}Co_{0.3}$-10% C;
▲- 75% g -10% $Mg_2Ni_{0.7}Co_{0.3}$-15% C;
*- 75% g -20% Mg_2Ni-5% C [22]

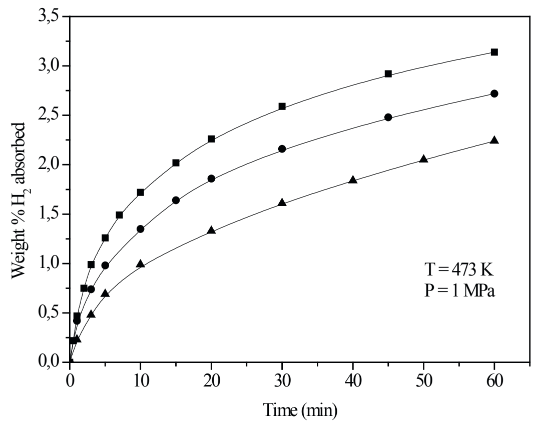


Figure 6. Kinetic curves of hydriding at 473 K and P = 1 MPa of the composites:
■ - 75% g -20% $Mg_2Ni_{0.7}Co_{0.3}$-5% C;
● - 75% g -15% $Mg_2Ni_{0.7}Co_{0.3}$-10% C;
▲- 75% g -10% $Mg_2Ni_{0.7}Co_{0.3}$-15% C

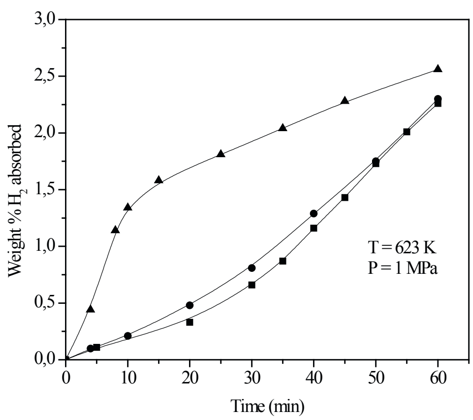


Figure 5. Kinetic curves of hydriding at 623 K and P = 1 MPa of the composites:
■ - 75% g -20% $Mg_2Ni_{0.7}Co_{0.3}$-5% C;
● - 75% g -15% $Mg_2Ni_{0.7}Co_{0.3}$-10% C;
▲- 75% g -10% $Mg_2Ni_{0.7}Co_{0.3}$-15% C

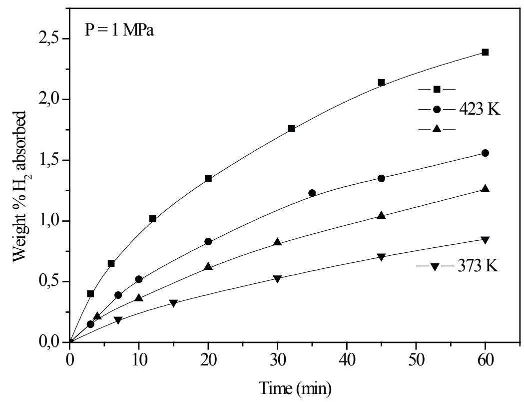


Figure 7. Kinetic curves of hydriding at 423 K and P = 1 MPa of the composites:
■ - 75% g -20% $Mg_2Ni_{0.7}Co_{0.3}$-5% C;
● - 75% g -15% $Mg_2Ni_{0.7}Co_{0.3}$-10% C;
▲- 75% g -10% $Mg_2Ni_{0.7}Co_{0.3}$-15% C
▼- 75% g -20% $Mg_2Ni_{0.7}Co_{0.3}$-5% C at 373 K and P = 1 MPa;

are shown in Table 1. The specific surface area slightly increases with the augmentation of the carbon content, which is more obvious with hydrided samples and is confirmed by electron microscopy. On the other hand, it should be taken into account that the duration of mechanical treatment is too short to cause a drastic change in specific surface area.

Figs. 4-7 show the kinetic curves of hydriding of composites with the same magnesium content and different concentrations of $Mg_2Ni_{0.7}Co_{0.3}$ and graphite at different temperatures and a pressure of 1 MPa. The theoretical capacity of the composites with 5, 10 and 15 wt% C is 6.42, 6.24 and 6.06 wt%, respectively. As is evident from the plots, the experimentally obtained maximum values of the composite capacities at 573 K for 60 min are 4.82, 4.58 and 4.59 wt% H_2, respectively. All composites exhibit improved kinetics at the beginning of the hydriding process. As a result, about 3.8 wt% of hydrogen is absorbed in 10 min. A similar behaviour was observed in earlier publications [32], the accelerated hydriding at the beginning of the absorption process being accompanied by a faster formation of a hydride

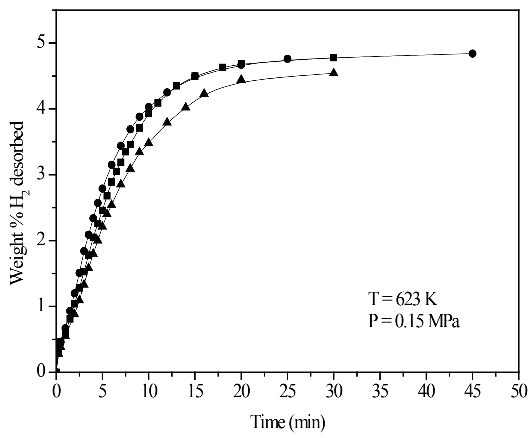


Figure 8. Kinetic curves of hydrogen desorption at 623 K and P = 0.15 MPa of the composites:
■ - 75% g -20% $Mg_2Ni_{0.7}Co_{0.3}$ -5% C;
● - 75% g -15% $Mg_2Ni_{0.7}Co_{0.3}$ -10% C;
▲ - 75% g -10% $Mg_2Ni_{0.7}Co_{0.3}$ -15% C

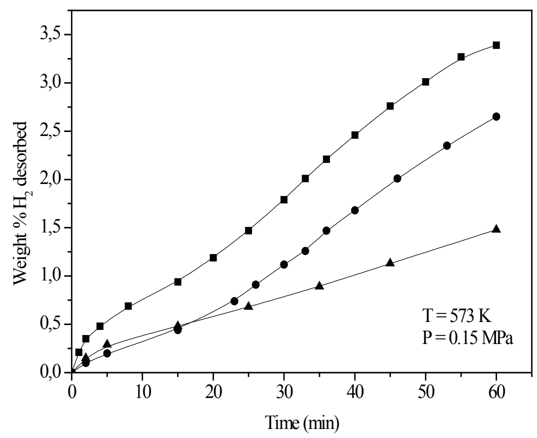


Figure 9. Kinetic curves of hydrogen desorption at 573 K and P = 0.15 MPa of the composites:
■ - 75% g -20% $Mg_2Ni_{0.7}Co_{0.3}$ -5% C;
● - 75% g -15% $Mg_2Ni_{0.7}Co_{0.3}$ -10% C;
▲ - 75% g -10% $Mg_2Ni_{0.7}Co_{0.3}$ -15% C

layer. This layer acts as a diffusion barrier so that it is impossible to attain absorption capacity close to the theoretical. Another reason for the lower capacity is the presence of MgO in the composites.

The highest capacity at 573 K (Fig. 4) is found with the composite having the lowest graphite content (4.82 wt%) due to the presence of a larger amount of $Mg_2Ni_{0.7}Co_{0.3}$ which is also hydrided under these conditions. The high absorption capacity and the improved hydriding kinetics are due to the presence of the intermetallic phase. The catalytic effect of the additive is associated with the formation of Mg_2NiH_4, this leading to an interface increase. The availability of Co clusters on the sample surface (proved in previous works, [14,32]) which act as active sites during dissociative hydrogen chemisorption also affects the kinetics favourably. Comparison of our previous investigations [24] with these results shows that they are poor, except of the early stage of the hydriding process. The difference between the hydrogen sorption characteristics of Mg-Mg_2Ni-C and Mg-$Mg_2Ni_{0.7}Co_{0.3}$-C composites probably can be explained by the use of another graphite and different Mg_2Ni type of additive.

During hydriding at 623 K of the composite 75 wt% Mg -10 wt% $Mg_2Ni_{0.7}Co_{0.3}$ - 15 wt% C, where the triple intermetallic compound does not participate in the process (Fig. 5), the effect of the larger amount of graphite on the composite behaviour is clearly visible. This can be ascribed not only to the increase in specific surface area as a result of the antisticking effect of carbon, but also to its ability to prevent the restoration of the oxide layer on the surface, thus eliminating the undesired effect of this layer on the dissociative chemisorption of hydrogen. Relatively good kinetics and a significant capacity are demonstrated by the three composites at 473 and 423 K (Figs. 6, 7), here again the composite with 5 wt% C having the highest capacity (3.14 and 2.39 wt%, respectively). This composite is also hydrided at 373 K, attaining a capacity of 0.85 wt%. It can be concluded that the Mg_2Ni type additive has a more pronounced effect on the hydriding kinetics at lower temperatures.

Figs. 8 and 9 illustrate the curves of hydrogen desorption of the three composites at 623 and 573 K and a pressure of 0.15 MPa. Before dehydriding, all composites were hydrided at 573 K. At 623 K they have significantly improved hydrogen desorption kinetics, almost the whole amount of absorbed hydrogen being desorbed in 30 min. At 573 K the dehydriding process during the first 5 min is accelerated, which is evidenced by the break in the curves (Fig. 9). This is due to the participation in hydrogen evolution at the begining of the process mainly of ternary hydride Mg_2NiH_4, which is less stable than MgH_2. The gas-solid interface increases as a result of presence of a few phases- MgH_2, Mg_2NiH_4 type hydride and $MgNi_2$, which leads to facilitation of the back diffusion of hydrogen. At 573 K, with the augmentation of the amount of graphite in the composites, the desoprtion kinetics decrease. As we mentioned in our previous work, it can be assumed that two opposite processes take place during hydriding of the graphite modified composites: destruction of the oxide layer and blocking of part of the surface by graphite. When the quantity of graphite is higher, it will block a larger part of the surface. It should be noted that when the quantity of graphite in the composite increases, the $Mg_2Ni_{0.7}Co_{0.3}$ content decreases. The increased content of $Mg_2Ni_{0.7}Co_{0.3}$, affects more favorably the hydrogen desorption kinetics of the composites at 573 K.

The difference in amounts of hydrogen adsorbed and desorbed by the three composites is due to the different content of $Mg_2Ni_{0.7}Co_{0.3}$ in them.

4. Conclusion

The results obtained on the absorption/desorption characteristics of mechanically activated composites 75 wt%Mg – (10, 15, 20) wt% $Mg_2Ni_{0.7}Co_{0.3}$ - (15, 10, 5) wt% C show a positive effect of the presence of the intermetallic compound and the graphite, which is mainly evidenced by improved kinetics at all hydriding/dehydriding temperatures in the present study. Only the composite 75 wt% Mg - 20 wt% $Mg_2Ni_{0.7}Co_{0.3}$ - 5 wt% C has shown hydrogen absorption at 373 K. The composites do not reach their theoretical capacity probably because of the accelerated kinetics causing early formation of the hydride layer, which makes hydrogen diffusion to the sample bulk difficult. Another reason could be the possibility of blocking the surface partially by graphite, this way hindering the access of hydrogen to it. The other possible reason for the lower capacity of the composites is the presence of a MgO layer on their surface. The combination of the additives- $Mg_2Ni_{0.7}Co_{0.3}$ and graphite has shown a more pronounced positive effect on the magnesium sorption kinetics toward hydrogen at lower temperatures of the triple intermetallic compound. The maximum capacity of the composites obtained by us as well as the temperature of desorption cannot satisfy the high requirements of the practice.

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