THE EFFECT OF THE MAX-PHASE Ti₃AlC₂ ON HYDROGEN STORAGE PROPERTIES OF Mg

Dr. Kirian I., Dr. Lakhnik A., Dr. Vyynash V., Prof. Dr. Rud A.
G.V. Kurdyumov Institute for Metal Physics NAS of Ukraine, Kiev, Ukraine
E-mail: kiryan.inna@gmail.com, lakhnik@imp.kiev.ua, vyynash@gmail.com, rud@imp.kiev.ua

Abstract: The MAX-phase Ti₃AlC₂ was synthesized by sintering method. The study of sorption properties of the sample was carried out under conditions of continuous heating. It was established that desorption of hydrogen begins at a temperature of ~210 °C. After complete desorption, the sample was re-heated in an atmosphere of hydrogen. It was found that Mg-5 wt% Ti₃AlC₂ composite begins absorb hydrogen at a temperature of ~76 °C. As a result of cycling, the temperature of desorption has shifted towards lower values ~186 °C.

KEYWORDS: MAX-PHASE, Ti₃AlC₂, HYDROGEN STORAGE

1. Introduction

The last years more attention is a pay to the search of the clean energy sources. The most promising area in this field is hydrogen power. Developing safe, efficient and affordable approaches of hydrogen storage is especially important for practical application. Compared to gaseous or cryogenic methods [1], the storage of hydrogen in a bonded state in the form of various compounds attracts great attention due to their unique characteristics, safety and high volumetric energy density. Metal hydrides attract a special attention [2]. Metal-hydrogen compounds have a high mass and volumetric density of hydrogen. However, the hydrogen content of the vast majority of hydrides is ~2%, which makes them economically unprofitable. Moreover, the temperature at which the release of hydrogen for the vast majority of hydrides is several hundred degrees. Hydrides based on intermetallic compounds exhibit significantly lower desorption temperatures of hydrogen. But their hydrogen capacity is small and does not exceed 1-2%. In contrast to the materials pointed out above, magnesium capable to absorb up to 7.67% hydrogen. Therefore magnesium is a most promising material for use in hydrogen energetic [3]. But there are crucial disadvantages must be overcome for widespread use of magnesium as a hydrogen storage media: high storage/release temperatures, slow hydrogen sorption/desorption kinetics and low cyclic stability. A wide range of different methods has been applied over the past decades. Mechanical grinding magnesium with a various additives cause a great practical interest since allows to synthesize high active powders with improved hydrogen sorption/desorption kinetics [4-7]. Further development of this approach may be the use of new type of catalysts - MAX phases [8] and their derivative 2D structures – MXene [9-11]. To prepare magnesium based hydrogen storage materials the ball milling under hydrogen atmosphere [12, 13] (so-called reactive grinding) is also widely used.

In this paper we propose to use the MAX-phase Ti₃AlC₂ as a catalyst additive to the magnesium powder. The samples were prepared by reactive ball milling under hydrogen atmosphere.

2. Materials and method

The MAX-phase Ti₃AlC₂ was synthesized by sintering method. The initial powders Ti, Al and spectrally pure graphite in atomic ratio of 3:1:1:2 with additive 5 wt% B₂O₃ were homogenized using the laboratory planetary ball mill Fritsch Pulverisette P-6 for 1 h. The milling speed was 200 rpm. The balls to powder ratio was 10:1. Then the homogeneous mixture was cold-pressed under 640 MPa and sintered at 1400 °C during 1 hr in Ar atmosphere.

Samples Mg-5 wt% Ti₃AlC₂ were prepared by ball milling under hydrogen atmosphere at 400 rpm for 10 hr. Initial hydrogen pressure in the milling vial was ~1 MPa. Every two hours the grinding process was stopped and a new portion of hydrogen gas was added. This technique allowed the control of the hydrogen absorption process. During grinding the mixture exhibited high activity of interaction with hydrogen.

X-ray diffraction studies are carried out on the standard diffractometer HZG-4 with filtered CoKα radiations in the Bragg-Brentano geometry. Rietveld refinement of the XRD patterns was performed by the MAUD software [14]. Investigation of the hydrogen sorption properties of the magnesium based composites was performed out on a homemade Sievert’s type apparatus.

3. Result and discussion

The diffraction pattern of synthesized MAX-phase Ti₃AlC₂ is shown on the Fig. 1. From the Rietveld refinement has been found that the sintered pellets contain ~98.5 wt% of Ti₃AlC₂ phase and ~1.5 wt% TiC.

![Fig. 1 XRD pattern of MAX-phase Ti₃AlC₂.](image_url)
The sorption properties of the composite Mg-5wt% Ti₃AlC₂ after reactive ball milling have been tested by the Sievert’s technique. A powder sample was placed in a reactor. Then as-milled sample was continuously heated from the room temperature up to 400 °C to estimate quantity hydrogen absorbed during the reactive grinding. After the first heating cycle from thermal desorption curve it was found that the decomposition of magnesium hydride starts at 210 °C and finished at a temperature of 310 °C (Fig. 3, a). As a result of cycling, the temperature of desorption is shifted towards the lower values of 186 °C (Fig. 3, b). The amount of hydrogen released from the sample under these conditions is about 4.8%. The release of hydrogen occurs in a wide range of temperatures. It could be seen use Ti₃AlC₂ MAX-phase as catalyst additive promotes to a remarkable decrease in the hydrogen desorption temperature from the magnesium hydride. It is one of the important moments at the development of materials for hydrogen energy. According to the literature data, the temperature of the beginning of decomposition of magnesium hydride is ~ 283 °C [15].

The studies of the hydrogen desorption kinetics under isothermal conditions at a temperature of 300 °C have been carried out. It was shown that the Mg-5wt.% Ti₃AlC₂ composite at this temperature desorption 4.5% hydrogen for 200 s (Fig. 5).

After complete desorption, the sample was re-heated in an atmosphere of hydrogen. From the sorption curve (Fig. 4) was established that Mg-5 wt% Ti₃AlC₂ composite begins absorb hydrogen at a temperature of ~ 76 °C. The amount of hydrogen absorbed after full saturation is 4.8%. It is corresponds to the amount of desorbed hydrogen.

The X-ray diffraction pattern of the composite Mg-5wt.% Ti₃AlC₂ after saturation is show on Fig. 6. According to the results of the phase analysis it is established that after the last saturation cycle the materials contains mainly MgH₂ with the preservation of the initial MAX-phase Ti₃AlC₂ and a
relatively small amount of MgO. Magnesium oxide was formed as a result of oxidation of the sample during X-ray diffraction studies in the air.

4. Conclusion

The use of the MAX-phase Ti$_3$AlC$_2$ as an active additive to magnesium at reactive ball-milling treatment results in the formation of a composite with a sorption/desorption temperature of ~ 76 °C /186 °C, which is significantly lower than that of pure magnesium hydride.

The hydrogen capacity of the composite Mg-5wt.% Ti$_3$AlC$_2$ is 4.8%.

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6. References

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