Preparation of Magnesium Silicide from Recycled Materials for Energy Storage.

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PREPARATION OF MAGNESIUM SILICIDE FROM RECYCLED MATERIALS FOR ENERGY STORAGE

Bumba J., Dytrych P., Solcova O., Kostejn M., Fajgar R., Maleterova Y., Kastanek F.

Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Rozvojova 135, 16502, Prague, Czech Republic, fax: +420220920661, tel: +420220390278, bumba@icpf.cas.cz

Abstract

Recycling technologies help to save energy, materials and environment. This is the main reason of their popularity. The recovery of semiconductors and metals depends on recycling treatment. A new multi-step technology, which enables to obtain pure silicon and hydrogen from waste materials, is reported in this study. The only by-product is magnesium phosphate, which is a desired fertilizer. Magnesium silicide was successfully prepared from milled silicon photovoltaic (PV) panels and milled Mg obtained from the scrap. The formed magnesium silicide was then hydrolysed by phosphoric acid to form a mixture of silanes. Gaseous products (silanes) were separated by cooling below their boiling temperature by liquid nitrogen and then thermally decomposed by a hot wire, e.g. Pt. This treatment leads to pure silicon and hydrogen release. In this study a deep-in characterization by various methods (X-Ray diffraction, Raman spectroscopy, Scanning Electron Microscopy (SEM) with Energy Dispersive X- Ray spectroscopy (EDX), etc.) of prepared samples was also done to explain the individual influences, e.g. reaction temperature and atmosphere.

Introduction

Magnesium silicide is an inorganic binary compound of magnesium and silicon with formula Mg_2Si with a dark blue colour in a powder form. This eco-friendly material has multiple applications thanks to their physical, mechanical and chemical properties. It is well known, that it can be also used for preparation of silicon hydrides (silanes). Silanes, which can be prepared by acidic hydrolysis, are very reactive pyrophoric gases with formula Si_nH_{2n+2}. Their instability can be successfully used in preparation of ultrapure silicon and hydrogen by thermal decomposition[1,2]. PV panels represent packaged, connected assembly of solar cells. Solar PV panels constitute the solar array of a photovoltaic system that generates and supplies solar electricity in commercial and residential applications. There are only available some solar panels that are exceeding 19% efficiency. Owing to that a single solar module can produce only a limited amount of power, majority of installations contain multiple modules.

The photovoltaic system typically includes a panel or an array of solar modules, an inverter, and sometimes a battery and/or a solar tracker and an interconnection wiring. Recently, it has become very attractive, due to the PV panels utilize only energy of solar light, don't consume material resources and don't produce any noise and toxic gases. The life time of PV module usually lasts 20 - 25 years. After that most of parts including up to 97% of semiconductors (mainly Si) must be recycled. A large number of companies and non-profit organizations have been engaged in taking-back and recycling operations for end-of-life modules, nowadays. Recycling possibilities strongly depend on the kind of technology applied in module production[3].

Automotive industry is main source of recycled magnesium. Due to the lightest metals used for structural applications to reduce weight are magnesium alloys. Approximately 1/3 of magnesium ends like new scrap during fabrication of structural products. It is really inevitable to effectively use primary magnesium and to find an efficient recycling technology to keep endurable price of magnesium. Magnesium is expensive because of a high energy consumption process used for its production. The only processes used for magnesium production are electrolysis of magnesium chloride and silicothermic (Pidgeon process) using reduction of dolomite at high temperature. There are necessary about 35 kWh for kilogram of primary magnesium. On the other hand recycling of Mg needs only 3 kWh per kilogram[4].

Experimental

Silicon based modules: aluminium frames and junction boxes are dismantled manually at the beginning of the process. The module is then crushed in a mill and the different fractions are separated - glass, metals, plastics, Si, etc. At present moment it is possible to recover up to 95% of weight. This process can be performed by flat glass recyclers since morphology and composition of a PV module is similar to those flat glasses used in the building and automotive industry. Obtained silicon was then crushed to powder in a mortar. Powdered silicon was observed by X-ray Photoelectron Spectroscopy (XPS). It was found out less than 5% Si-O. Used powdered magnesium contained less than 3% Mg-O. The stoichiometric mixture of magnesium and silicon was loaded to silica tube and vacuum pump (or inert atmosphere) was connected. After 30 minutes of water and bounded gases desorption, tube furnace was turned on. The reaction temperatures were between 350 – 600°C. The pressure was maintained at about 30 Pa, which was a limitation of the used vacuum pump. The reaction time was 30 minutes. This reaction is described by equation:

$$2\,Mg + Si \rightarrow Mg_2Si \quad (350°C - 600°C/\ 30\ min.\ \textit{in vacuo})$$

Prepared magnesium silicide was then hydrolysed by aqueous phosphoric acid to produce silanes and magnesium phosphate as the only by-product. The hydrolysing reaction is described below:

$$Mg_2Si + H_3PO_4\,(aq.) \rightarrow Mg_3(PO_4)_2 + SiH_4 + Si_2H_6 + Si_3H_8 + iso\text{-}Si_4H_{10} + Si_4H_{10}$$

Evolved gas was condensed by liquid nitrogen and analysed by Gas Chromatography – Mass Spectroscopy (GC-MS). The silane was then controlled released into the cuvette with hot platinum wire. Decomposition of silane was observed by Fourier Transform Infrared Spectroscopy (FTIR). Deposition of silicon was obvious. The equation of thermal decomposition of silanes is expressed like:

$$Si_nH_{2n+2} \rightarrow n\,Si + (2n + 2\,)H_2$$

Results and Discussion

It was prepared dark blue powdered material (Figure 1). Raman spectroscopy (Figure 2) and SEM/EDX (Figure 3) confirmed that it is high homogenous magnesium silicide.

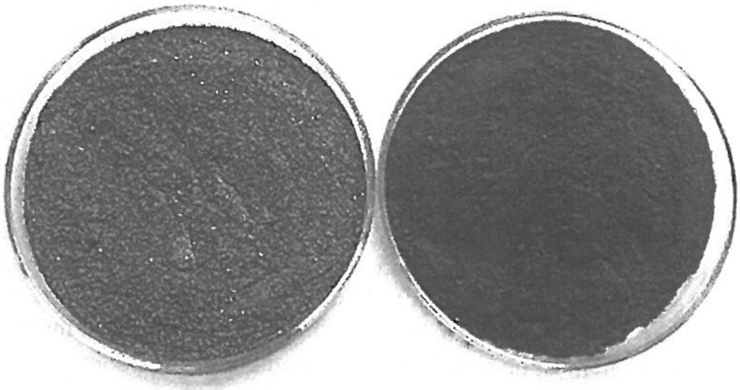

Figure 1. Mixture of starting materials (Mg + Si) (left); Prepared magnesium silicide (right).

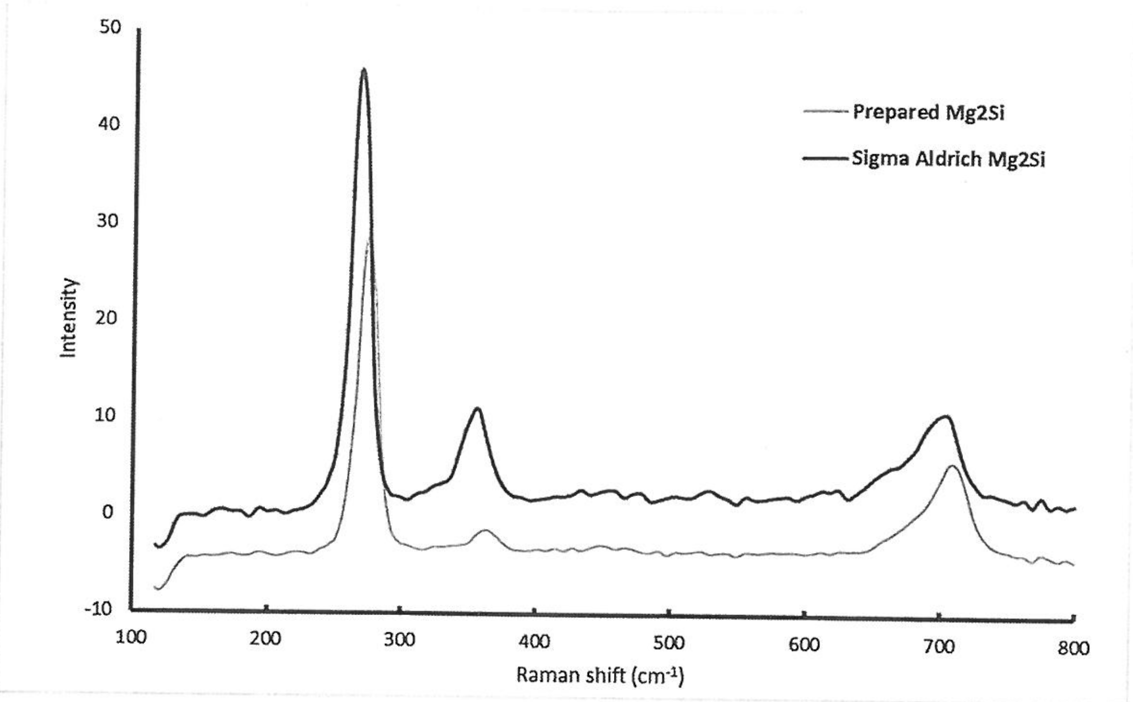

Figure 2. Comparison of standard magnesium silicide from Sigma Aldrich and prepared product.

Figure 2 shows that magnesium silicide was successfully prepared and SEM/EDX Figures 3 show very small particles and high homogenous product.

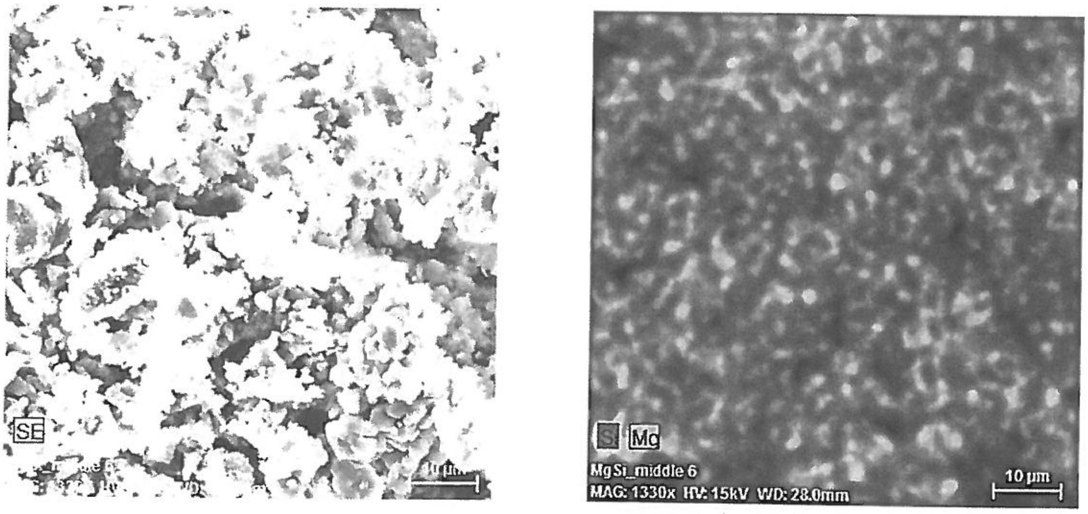

Figure 3. Prepared Mg_2Si (SEM) (left) and EDX (right)

The following Figure 4 shows products of silane decomposition. It is obvious that the main products are silane and disilane. Silane is a desired product for hydrogen production with respect to the ratio between hydrogen and silicon.

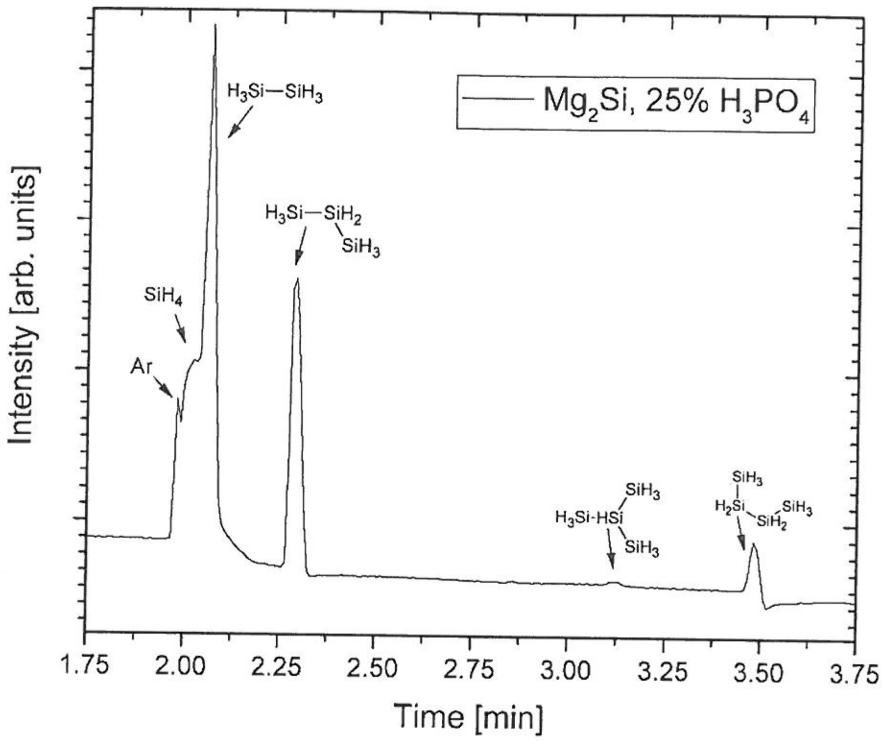

Figure 4. Production of silanes by hydrolysis of magnesium silicide with 25% H_3PO_4 (GC-MS).

Thermal decomposition of silane is demonstrated as a function of silane decreasing in time. Decreasing of silane was observed by FTIR (Figure 5).

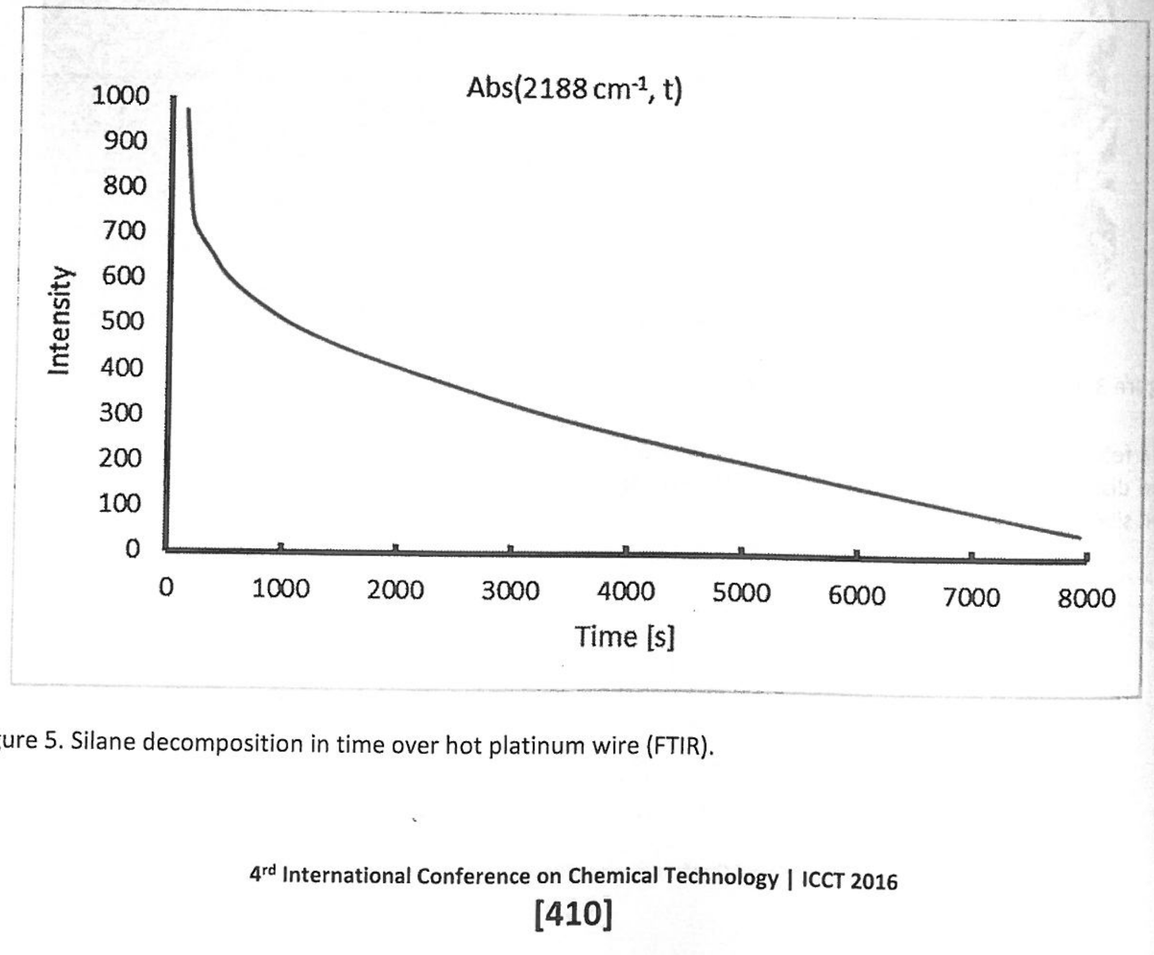

Figure 5. Silane decomposition in time over hot platinum wire (FTIR).

Conclusion

Magnesium silicide was successfully prepared by reaction of milled silicon from PV panels with milled Mg from scrap. It was confirmed by comparison of Raman spectra of standard and prepared material. SEM/EDX analysis showed that prepared magnesium silicide is really highly homogenous. The major product of subsequent hydrolysis of formed Mg_2Si was a mixture of silanes with majority of silane. In fact, silane is the optimal product for hydrogen production thanks to the best ratio between hydrogen and silicon. The only by-product of hydrolysis is magnesium phosphate, a desired fertilizer. The gaseous silanes were successfully separated (cooled) and thermally decomposed with formation of pure Si and H_2. Deposition of pure silicon, which can be used as a material for new PV panels or other semiconductor components, was indirectly confirmed by FTIR.

Acknowledgement

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