Hydrogen, as a clean and renewable energy carrier, has the potential to play a significant role in transition towards a low-carbon economy and the mitigation of climate change. Developing high-capacity, solid-state hydrogen storage materials is critical for large-scale hydrogen deployment. Magnesium hydride (MgH_2), with a theoretical hydrogen storage capacity of 7.6 wt%, is an attractive candidate due to its high hydrogen affinity, low cost and abundance. But high enthalpy of formation of MgH_2 and high decomposition energy of MgH_2 requiring about 76 kJ/mol of heat for each mole of H_2 released lead to increase of hydrogenation temperature, slowing the hydrogenation and dehydrogenation kinetics [1,2]. Ni is often used as a catalyst to improve the kinetics of MgH_2 formation in H_2-contained atmosphere due to reduced enthalpy of formation of Mg-Ni alloys (<65 kJ/mol) and reduced activation energy of dissociation of molecular hydrogen in comparison to Mg [1,2,4]. Nanostructuring of Mg/Ni coatings by increasing the density of Mg/Ni interfaces improves the hydrogenation/dehydrogenation kinetics of MgNi films [2]. Further improvement of dehydrogenation of magnesium hydride-based material can be achieved by using non-thermal activation of the metal hydride compound via laser irradiation which can provide more efficient dehydrogenation at lower temperatures [3]. It is shown that MgH_2-based films are partially transparent with low electrical conductivity, letting the laser beam photons to reach the bulk MgH_2-based material deep into the thin film layer [4]. Laser irradiation test setup is shown in Fig. 1.

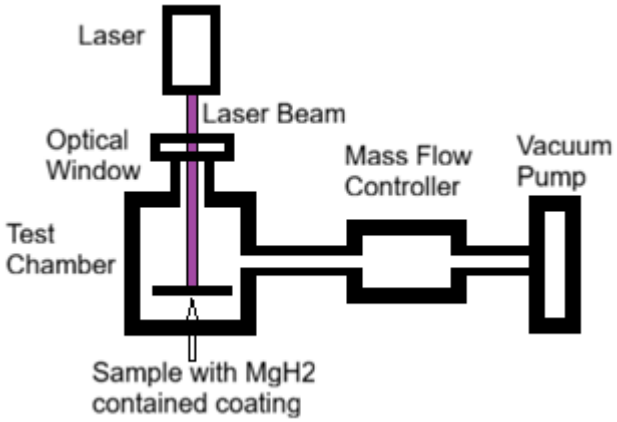

Figure 1. Laser irradiation test setup.

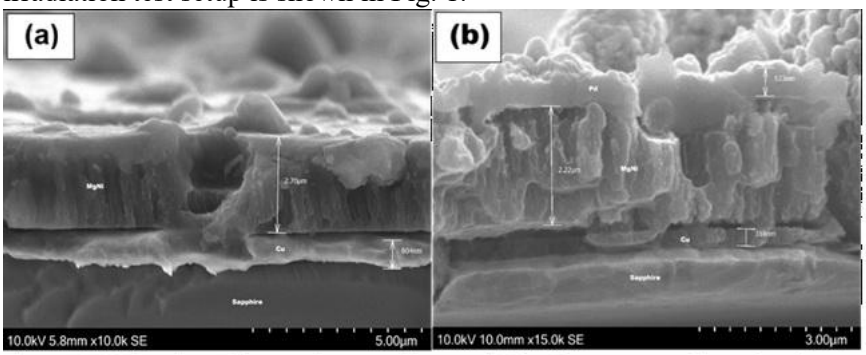

Figure 2. MgNi coating with copper bottom sublayer and Pd top layer over sapphire wafer substrate deposited with arc current of 70A: (a) before furnace hydrogenation; (b)-after furnace hydrogenation.

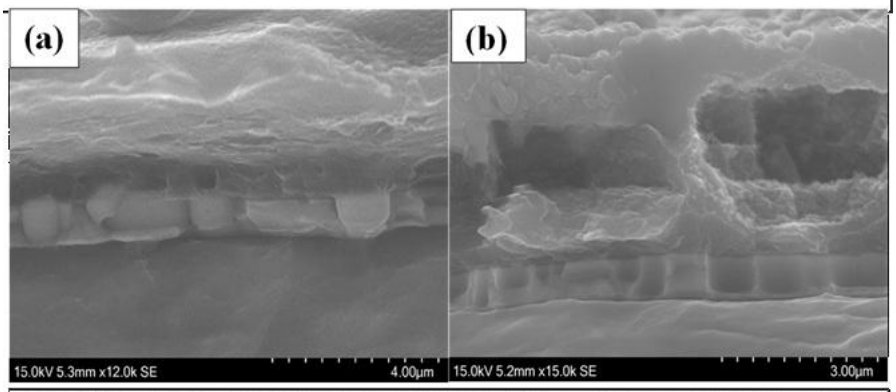

Figure 3. MgNi coating with NiTiCu bottom sublayer and Pd top layer over aluminum foil substrate deposited with arc current of 50A: (a)-before furnace hydrogenation; (b)-after furnace hydrogenation.

MgNi thin film coatings were prepared via vacuum cathodic arc deposition on sapphire wafer, aluminum foil (~25 mm thick), and aluminized polyamide tape. The cathodic arc process conditions for deposition of MgNi coatings were chosen to keep the substrate temperature low for which the arc current was selected from 50 to 70 A, and substrates (both sapphire and metal foil) were installed in a free-standing position at floating potential resulting in substrate temperature less than 300°C. Multielement cathodic arc coatings can be deposited from composite multielement target made by hot press sintering or from segmented targets. Segmented Mg/Ni cathode

target 75 mm dia with 7 Ni inserts, 8 mm dia x 12 mm long, was used for deposition of MgNi thin film coating. In this approach, the cathodic arc spots are residing both on Mg and Ni surface, while the residence time on Mg surface is order of magnitude longer than that on Ni inserts because the minimal arc current supporting the stationary cathodic arc spot on Mg is much smaller than that on Ni. This results in creating a small, nano-scale inclusion of Ni in the Mg thin film coating, increasing the Mg/Ni interfaces [2]. The supportive NiTiCu bottom sublayer was deposited from the composite Ni50Ti48Cu2 cathode target made by hot press sintering. Based on Movchan-Demchishin zone diagram, the microstructure of PVD coating is defined by the parameter $s=T_s/T_m$ where T_s is substrate temperature, T_m is melting point [5]. Under our coating deposition conditions (T_s<300°C) the NiTiCu supportive sublayer with s<0.1 growth in Zone 1 while MgNi layer with s>0.3 growth in Zone 2. Zone 1 is characterized by large open columns while zone 2 is characterized by narrow coalescent closed columns as demonstrated in coating cross-sections in Figure 3. The open columnar structure of the NiTiCu sublayer is promoting the larger columnar growth of the main MgNi layer and also developing the open voids favorable for hydrogen transport both in hydrogenation and dehydrogenation stages. The layer of Pd with thickness <~100 nm was deposited on top of cathodic arc MgH_2 thin film coating via e-beam evaporation to improve the hydrogenation kinetics of MgNi films in H_2-contained atmosphere. The hydrogenation of the MgNi films was performed in Ar95% + $H_2$5% environment at 300°C in atmospheric pressure. The columnar structure and voids survived during the hydrogenation stage as illustrated in Figures 2,3. At the same time, the hydrogenation changed the color of the coating surface from silver metal color to dark color accompanied by reduced electrical conductivity and increased light transparency of the film indicating shift from metallic to insulative ceramic [4].

Laser dehydrogenation testing in experimental setup shown in Fig. 1 demonstrated that almost 90% of hydrogen contained in hydrogenated NiTiCu/MgNi/Pd coating can be released by CW laser irradiation from the 1" x 1.25" sample [3]. The hydrogen flow generated by laser irradiation of one hydrogenated coating spot 1mm x 10mm during 1s is ranging from 0.5 to 1 SCCM. Without moving the laser, we extended the spot size by reflection (and duration) and widened the irradiation area to continue the release. At 2 seconds we had a wide field flow rate of 0.825 SCCM which then fell off quickly. In testing of CW laser irradiation of hydrogenated coating in vacuum, it was found that hydrogen is released both in the form of atomic hydrogen H and molecular hydrogen H_2 as a result of hydrogen emitting from the MgH_x compound (including microcrystalline MgH_2 and Mg/H solid solution) which then can partially collisionally recombine predominantly on Ni particles [4] and on chamber's walls creating molecular hydrogen H_2 as illustrated in RGA chart of partial pressure as a function of time in Figure 4. The partial light transparency and increased light absorbance of MgH_2 improved by columnar microstructure with open voids provide a basis for using amplified light beam to release hydrogen from the thin film, contributing to safe and efficient hydrogen storage.

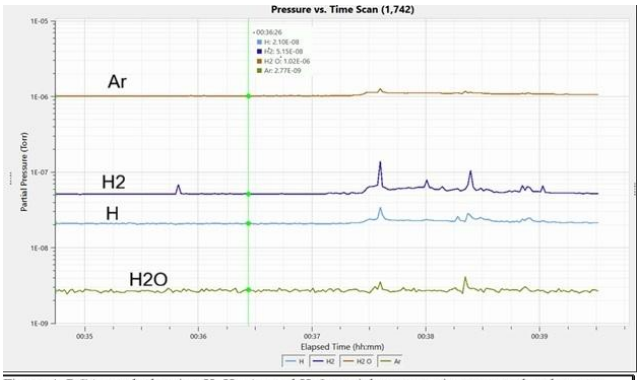

Figure 4. RGA graph showing H, H_2, Ar, and H_2O partial pressures in vacuum chamber as a function of time during laser desorption treatment of MgH_2-contained coating.

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