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An improvement in the properties of hydrogen storage alloy by copper microencapsulation

Seong Sik Moon, Kee Suk Nahm *
Dept. of Chemical Technology, College of Engineering, Chonbuk National University, Chonju 560-756, South Korea

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Abstract

A hydrogen storage alloy of $LaNi_5$ was microencapsulated by electroless chemical plating with metallic copper. The surface morphology of the microencapsulated $LaNi_5$ was studied for different electroless plating conditions. The deactivation, regeneration, and catalytic activity of $LaNi_5$ were compared before and after the microencapsulation. The amount of Cu deposited on the $LaNi_5$ surface increased with increasing concentration of the plating solution. A relatively smooth morphology was obtained by decreasing the plating rate. The extent of the deactivation of the microencapsulated $LaNi_5$ was very low compared to that of $LaNi_5$ and decreases with the number of the microencapsulation. Almost complete regeneration was achieved for microencapsulated $LaNi_5$, but the extent of the regeneration decreased with the number of regeneration cycles at higher temperatures. The microencapsulated $LaNi_5$ showed a higher catalytic activity for methanation of carbon monoxide, where the conversion was almost quantitative.

Keywords: Microencapsulation; Hydrogen storage alloys; Electroless plating

1. Introduction

Hydrogen storage alloys, which are a kind of intermetallic compounds, have received much attention owing to their importance in applications such as hydrogen and thermal reservoirs, heat pumps, compressors, batteries, hydrogen purification and recovery devices, etc. [1–3]. The alloys have also been found to be fairly active as catalysts in hydrogenation and dehydrogenation of organic compounds because they absorb and desorb hydrogen rapidly in the atom form [4,5]. However, there are some difficulties that impede the industrial applications of the alloys. The main hindrance in the application of the alloys are pulverization to very fine powder, poor thermal conductivity of the powdered alloys, and poor resistance to poisoning by gaseous impurities such as O_2, CO, or H_2O in hydrogen [3].

Various technologies have been explored to solve these problems [6–8]. Among them, it has been known that the microencapsulation of the powdered alloys with metallic copper or nickel using the electroless plating technique is a promising candidate for overcoming these problems. The microencapsulation has significantly improved the characteristics of hydrogen storage, thermal conductivity and deactivation of the hydrogen storage alloys [9–11]. However, there are very few detailed studies on the surface morphology and the deactivation of microencapsulated alloys prepared at various plating conditions and the regeneration of the deactivated alloys.

In this work, we have investigated the surface morphology of $LaNi_5$ particles microencapsulated with metallic copper at various electroless plating conditions such as composition and pH of plating solution, and plating temperature. The deactivation of microencapsulated $LaNi_5$ was examined with carbon monoxide in hydrogen gas. The regeneration condition of the deactivated sample was also studied. Finally, the catalytic activity of microencapsulated $LaNi_5$ was tested for methanation of carbon monoxide.

2. Experimental

2.1. Sample

The hydrogen storage alloy used in the present experiments was $LaNi_5$ purchased from the MPD Technology Co. Hydrogen with a normal purity of 99.9999% was used for the activation of $LaNi_5$ and the preparation

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* Corresponding author.

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of mixed gas without further purification. A mixed gas of CO and H_2 was used to investigate the deactivation and the catalytic activity of $LaNi_5$ and microencapsulated $LaNi_5$. Chemicals of reagent grade and deionized water were used for the preparation of the plating solutions.

2.2. *Microencapsulation of $LaNi_5$ powders*

The purchased $LaNi_5$ particles (about 300 μm) were further pulverized by repeated hydrogen absorption–desorption cycles more than 20 times as described in the literature (see Fig. 1(a)) [12]. $LaNi_5$ particles of 30 g were first charged in the reactor, evacuated up to 10^{-2} Torr for 30 min at 303 K, and pressurized with 30 atm hydrogen gas for 1 h. The size of $LaNi_5$ particles after the repeated sorption process was less than 10 μm (see Fig. 1(b)).

For the microencapsulation of the powdered $LaNi_5$, the surface of the $LaNi_5$ powders (5 g) was degreased in an ultrasonic cleaner containing acetone for 10 min, washed with deionized water 5 times, and filtered. The resulting sample was dried at 333 K for 24 h in an oven. For the formation of initial nuclei on the $LaNi_5$ surface, the dried $LaNi_5$ was immersed and stirred for 5 min in a mixed solution of deionized water (120 ml) and 36% HCl solution (40 ml) in which $SnCl_2$ (1.5 g) and $PdCl_2$ (0.02 g) were dissolved. After stopping the agitation and removing the solution from the beaker, the remaining $LaNi_5$ powders were lightly washed with deionized water and stabilized with 10% H_2SO_4 aqueous solution. The powders were again washed with deionized water, filtered through filter paper, and dried. The pretreated $LaNi_5$ powders were weighed up to 0.1 μg.

The chemical plating solution for the microencapsulation of $LaNi_5$ powders was prepared from $CuSO_4$ (10.0 g l^{-1}), HCHO (2.5 g l^{-1}), $C_{10}H_{14}O_8N_2Na \cdot 2H_2O$ (30.0 g l^{-1}) and H_2NCH_2COOH (3.0 g l^{-1}) aqueous solutions. Such composition of the solution is defined as 100% in the following. Formaldehyde was used as a reducing agent in the plating reaction. The amount of each chemical species in the 100% plating solution was varied for the preparation of 50, 200 and 300% solutions. The powdered $LaNi_5$ particles were microencapsulated with copper in the plating solution of 1 l at 70 °C and pH = 12.2. The pH of the plating solution was controlled by the addition of NaOH aqueous solution. The microencapsulated $LaNi_5$ powders were washed with deionized water more than 10 times and dried. The amount of Cu deposited on $LaNi_5$ surface was measured from the weight difference of the $LaNi_5$ powders before and after the microencapsulation.

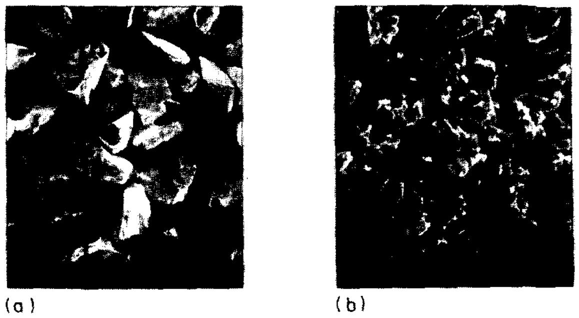
(a) (b)

Fig. 1. Scanning electron micrographs of (a) unactivated $LaNi_5$ and (b) activated $LaNi_5$.

2.3. *Experimental apparatus and procedures*

Fig. 2 shows an experimental apparatus used for the test of the deactivation, regeneration, and catalytic activity of the microencapsulated $LaNi_5$. The experimental apparatus was built up with stainless steel (sus-316) pipe of 1/4 in and needle valves. A test sample of 0.7 g (based on $LaNi_5$) was loaded in a reactor, which is made of a stainless steel pipe of 60 mm high and 1/4 in diameter. Both ends of the tube were sealed with a stainless steel filter (1250 mesh) to prevent the loss of the $LaNi_5$ powders from the reactor. A cylindrical type filter was also placed on the inside wall of the reactor to permit hydrogen to diffuse well into the powdered $LaNi_5$ bed. The reactor was heated by a temperature-controlled electric furnace. The experimental temperature was monitored with a C/A thermocouple of 1/16 in diameter positioned in the centre of the reactor in the furnace.

The deactivation and regeneration processes were examined in a batch reactor modified by closing valves 8 and 9 of Fig. 2. The extent of the deactivation and regeneration were estimated in terms of the reacted fraction of $LaNi_5$ by measuring the pressure drop in the reaction system owing to the absorption of hydrogen in the mixed gas by $LaNi_5$. The pressure was measured

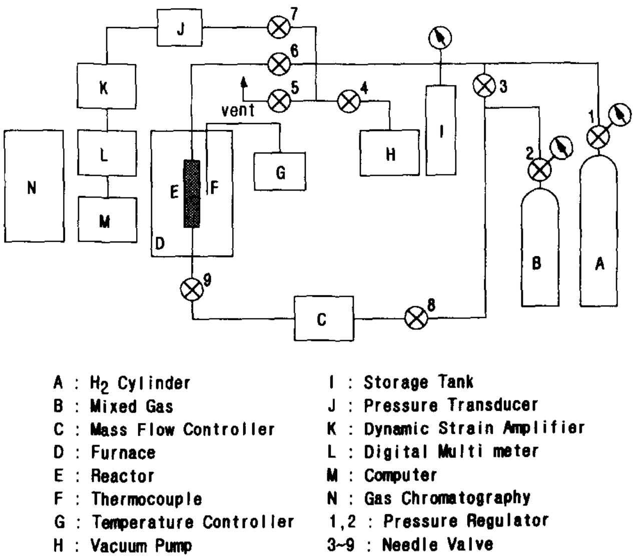

Fig. 2. Experimental apparatus for the test of the deactivation, regeneration and catalytic activity of the microencapsulated $LaNi_5$.

with a pressure transducer (TMI GDB-50K). The output of the pressure transducer was connected to a dynamic amplifier (TMI MD-1032) and recorded on an IBM PC through a digital multimeter (Fluke-45). The reacted fraction is defined as the mol. ratio of hydrogen absorbed at a given time to the total number of mol. of hydrogen that can be absorbed in pure $LaNi_5$ charged in the reactor [12].

The catalytic activity of the microencapsulated $LaNi_5$ for the methanation of carbon monoxide was studied in a fixed bed continuous flow reactor modified by closing valves 3 and 7 of Fig. 2. The reactant gas was supplied to the reactor with a mass flow controller (MKS 247C 4-channel control box and 1159B control head). The composition of gaseous products from the outlet of the reactor during the methanation was analyzed by gas chromatography (GC) equipped with thermal conductivity detector (TCD) using molecular sieve-5A (column: 4 mm X 2 m ss) as a column material. The carrier gas was nitrogen (55 ml min^{-1}) and the temperature of the column and TCD was 30 °C and 300 °C respectively.

3. Results and discussion

3.1. Microencapsulation of $LaNi_5$ powders with Cu

The $LaNi_5$ powders were microencapsulated by electroless chemical plating with copper in a batch reactor with varying of the plating conditions such as concentration and pH of the plating solution, plating temperature and the number of platings. The surface morphology of the microencapsulated $LaNi_5$ powders was examined with a scanning electron microscopy (SEM).

It was found that the microencapsulation of $LaNi_5$ powder with Cu occurs above 50 °C and pH 11. Hence, all the experiments were performed at a fixed temperature of 70 °C and pH of 12.2. Listed in Table 1 are the plating conditions and the wt.% of copper deposited after the plating for each run.

Scanning electron micrographs of the microencapsulated $LaNi_5$ powders are shown in Figs. 3–6. Fig. 3 shows the morphology of $LaNi_5$ powders microencapsulated at a given time at different concentrations of the plating solutions. The micrographs indicate that the surfaces of the $LaNi_5$ powders after the microencapsulation are coated completely with a Cu layer and small Cu particles begin to deposit on the microencapsulated surface at higher concentrations of the plating solution. This suggests that the Cu layer encapsulating the $LaNi_5$ powder particles consists of copper grains and the grain size is reduced with decreasing concentration of the solution, resulting in the formation of a soft surface. Increasing the copper concentration in the solution will lead to an increase of the plating rate. We believe that the grains are closely stacked at slower plating rates, leading to a soft surface. On the other hand, at faster plating rates, the grain size increases and small particles are formed, leading to the deposition of small particles on the $LaNi_5$ surface instead of closely stacked grains. The wt.% of Cu deposited on the $LaNi_5$ surface increases with the increase of the concentration of the plating solution.

In order to investigate the effect of the repeat number of the plating, a given concentration of the solution was decreased by diluting with an appropriate volume of deionized water and then $LaNi_5$ was microencapsulated a certain number of times. For instance, 1 l of the 300% plating solution was diluted to 3 l of 100% solution, and then the $LaNi_5$ powders were microencapsulated in each 1 l of the diluted solution (100%). This results in three times plating of the powder in 1 l of 100% solution. Fig. 4 shows micrographs for the surfaces of three times microencapsulated $LaNi_5$ powders in terms of the concentration of the plating solution.

The observed surface of the microencapsulated $LaNi_5$ has a relatively smooth morphology regardless of the concentration of the plating solution.

For a further detailed study of the effect of the repeat number on plating, the microencapsulation of $LaNi_5$ was carried out five or ten times in each 1 l of the diluted solution of the 100% plating solution. As shown in Fig. 5, micrographs of the microencapsulated $LaNi_5$ powders show that the surfaces become much more smooth as the number of platings increases. Therefore, it can be concluded that the repeated microencapsulation produces a smooth surface morphology in the microencapsulation of $LaNi_5$ powders. The above experiment shows that with lowering the concentration of the plating solution or increasing the number of the platings, the surface of the microencapsulated $LaNi_5$ becomes more smooth. The plating rate will be reduced

Table 1
The plating condition and the wt.% of copper deposited after the plating for each run

Composition, %	50	100	200	300	50	100	300	100	100	100	100	100
Plating number	1	1	1	1	3	3	3	5	10	1	1	1
Temperature, °C	70	70	70	70	70	70	70	70	70	40	50	70
pH	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	11
Cu wt.%	21.83	37.90	55.02	65.51	20.56	36.26	62.67	36.77	35.14	34.42	35.80	34.41

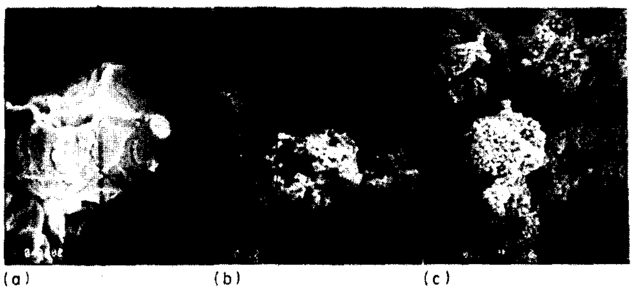
(a) (b) (c)

Fig. 3. Scanning electron micrographs of $LaNi_5$ powders microencapsulated for a time in (a) 50%, (b) 100% and (c) 300% plating solutions.

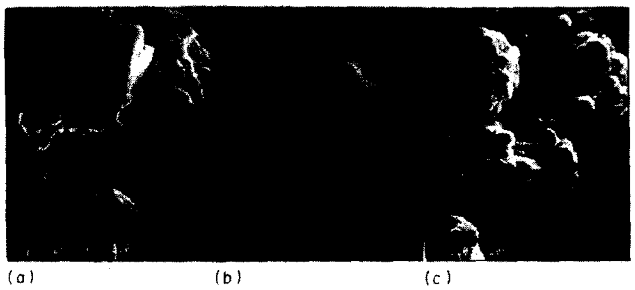
(a) (b) (c)

Fig. 4. Scanning electron micrographs of $LaNi_5$ powders microencapsulated three times in (a) 50%, (b) 100% and (c) 300% plating solutions.

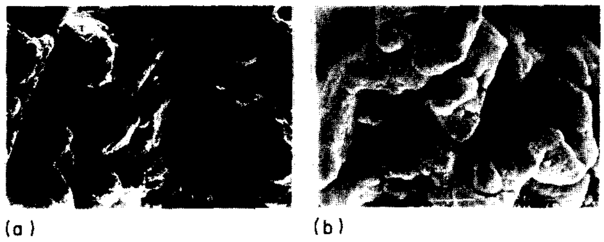
(a) (b)

Fig. 5. Scanning electron micrographs of $LaNi_5$ powders microencapsulated (a) 5 times and (b) 10 times in 100% plating solutions.

if the copper concentration in the solution decreases and/or the number of the plating increases. The formation of the smooth surface may be due to the reduction of the plating rate. The plating rate can also be modulated with adding an amount of the reducing agent (HCHO) because the microencapsulation proceeds only when the reducing agent is added to the plating solution at the plating conditions employed.

In order to see the effect of the plating rate on the microencapsulated surface morphology, the microencapsulation was performed with variations of the adding time interval of the reducing agent. The reactor was first charged with 1 l of the plating solution that does not contain the reducing agent, and then temperature and pH of the solution were adjusted to be 70 °C and 12.2 respectively. After introducing $LaNi_5$ powders into the reactor, agitating vigorously the plating solution, 6 ml of the reducing agent was introduced into the reactor 1 ml each time interval. Fig. 6 shows SEM images of the surfaces of $LaNi_5$ powders microencapsulated with varying time intervals. It is seen that the grain size of the copper layer is reduced with increasing time interval.

From the above experiments, it is clear that at lower plating rates the surface of the microencapsulated $LaNi_5$ powders retains a relatively smooth morphology, but small Cu particles deposit on the microencapsulated surface at higher plating rates. The surface morphology of the microencapsulated $LaNi_5$ powders can be controlled by variation of the plating rate, and the amount of Cu coating $LaNi_5$ after the microencapsulation is dependent on the concentration of the plating solution.

The surface of the microencapsulated $LaNi_5$ powders was analyzed by X-ray diffraction (XRD) using a $CuK\alpha_1$ target to confirm the deposited Cu. Shown in Fig. 7 are XRD spectra for the microencapsulated $LaNi_5$ in terms of the plating solution concentration. Fig. 7(a) represents the typical XRD spectrum taken from the pulverized $LaNi_5$. The main peaks of diffraction angle for $LaNi_5$ are observed at 2θ values of 30.56, 35.86, 42.64 and 45.64, while those for Cu at 43.34, 50.48 and 74.20 as shown in Figs. 7(b)–7(e). With increasing the concentration of the plating solution and the number of the plating, the intensity of the XRD peaks for Cu increases, whereas that for $LaNi_5$ decreases.

3.2. Deactivation of $LaNi_5$ by CO

The deactivation of the microencapsulated $LaNi_5$ powders was investigated by repeating the absorption–desorption cycle in hydrogen gas containing 200


(a) (b) (c)

Fig. 6. Scanning electron micrographs of $LaNi_5$ powders microencapsulated varying the adding time interval of the reducing agent (1 ml): (a) 5 min, (b) 10 min and (c) 20 min.

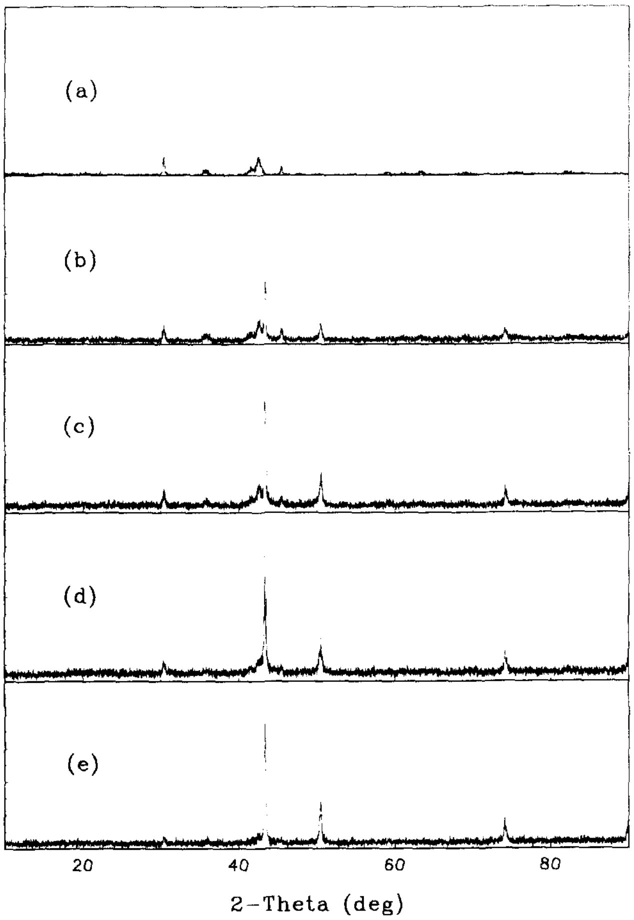

Fig. 7. XRD patterns of $LaNi_5$ powders before and after microencapsulation: (a) $LaNi_5$, (b) Cu–$LaNi_5$ (100%, 1 time), (c) Cu–$LaNi_5$ (200%, 1 time), (d) Cu–$LaNi_5$ (300%, 1 time) and (e) Cu–$LaNi_5$ (300%, 3 times).

ppm CO and compared with that of $LaNi_5$. The sample (0.7 g based on $LaNi_5$) was activated in the reactor by repeated pure hydrogen sorption cycles, and then evacuated under 10^{-2} Torr for 15 min to desorb the hydrogen remaining in the sample. The reaction system was pressurized with the mixed gas to the experimental pressure. Valve 6 of Fig. 2 was opened for the absorption of hydrogen in the mixed gas by the sample. The pressure drop in the reaction system was recorded with time by using the pressure transducer. When the pressure in the reaction system remained constant, unreacted gas in the system was released to the air. The sample was again evacuated under vacuum for 15 min and the above procedures were repeated. The pressure–concentration–temperature (P–C–T) curves which characterize the hydrogen absorption capacity of $LaNi_5$ were measured for the microencapsulated $LaNi_5$. The measured P–C–T curves of $LaNi_5$ before and after the microencapsulation were similar to those reported in the literature [9]. This result implies that the hydrogen absorption capacity of $LaNi_5$ does not change with microencapsulation. The deterioration of the hydrogen absorption capacity of the sample owing to the deactivation by CO in the mixed gas was measured in terms of the reacted fraction of the sample with the number of hydrogen absorption–desorption cycles.

$LaNi_5$ and microencapsulated $LaNi_5$ react with hydrogen gas containing 200 ppm CO at 303 K and 955 kPa of initial pressure. The reacted fractions of the samples are plotted as a function of the sorption cycle at four different plating solution concentrations as shown in Fig. 8. It is shown from the figure that both $LaNi_5$ and the microencapsulated $LaNi_5$ powders are deactivated with increasing the number of the cycles, but the extent of the deactivation of the microencapsulated $LaNi_5$ is very low compared to that of $LaNi_5$. It is probably because contact between CO and $LaNi_5$ surface is inhibited by the presence of the Cu layer on the $LaNi_5$ surface. The extent of the deactivation of the microencapsulated $LaNi_5$ varies slightly but is independent of the concentration of the plating solution used for the microencapsulation. According to the fact that the amount of the deposited Cu on the $LaNi_5$ particles increases almost linearly with concentration of the plating solution, the extent of deactivation should decrease linearly with the plating solution concentration if the crack density of the Cu film is independent of the amount of deposited Cu. As shown in Fig. 3, however, the grain size increases and leads to small Cu particle at higher concentrations of the plating solution, which will lead to an increase in the crack density of the Cu film. It can therefore be assumed that the extent of deactivation remains almost constant regardless of the concentration of the plating solution because both the thickness of the Cu film and the crack density increase as the concentration of the plating solution increases.

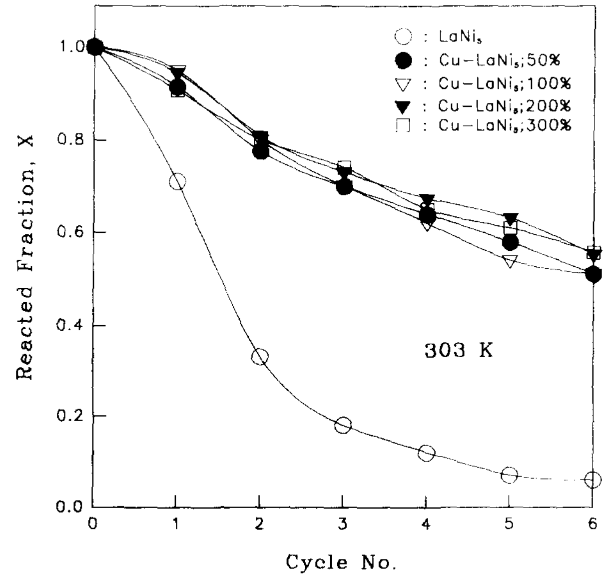

Fig. 8. Plots of reacted fraction vs. reaction cycle at 303 K and 955 kPa in hydrogen containing 200 ppm CO.

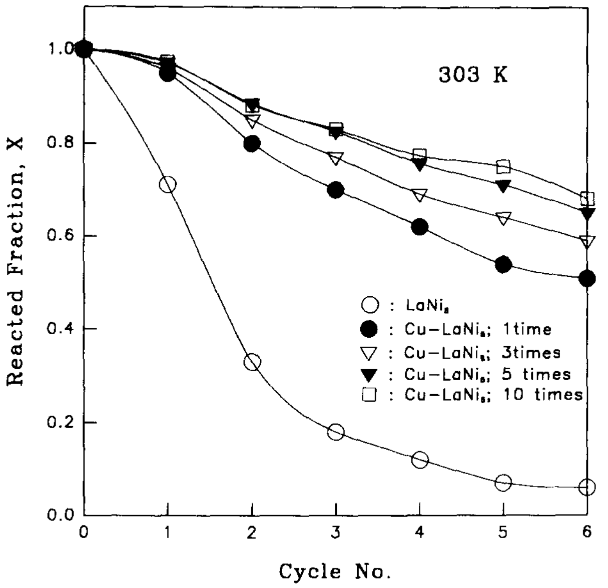

Fig. 9. Plots of reacted fraction vs. reaction cycle at 303 K and 955 kPa in hydrogen containing 200 ppm CO.

The effect of the number of the microencapsulations on the deactivation was investigated as a function of the sorption cycles. The microencapsulation was carried out by increasing the number of microencapsulations. It can be clearly seen from Fig. 9 that the deactivation decreases with the number of microencapsulations. The analyses of SEM and XRD indicate that with increasing the number of microencapsulations, $LaNi_5$ was well microencapsulated with Cu and the intensities of the Cu related peaks increase. Hence, the result in Fig. 9 is because the crack density is reduced with increasing the number of the platings, and accordingly the Cu layer covering $LaNi_5$ inhibits the deactivation of $LaNi_5$ with CO in the mixed gas. But a complete removal of the deactivation could not be achieved, even for the case of ten times microencapsulation. This implies that the Cu layer has very small cracks which can not be observed with SEM. It is confirmed from the above results that the deactivation of $LaNi_5$ powders owing to CO can be reduced significantly by microencapsulation with Cu.

3.3. Regeneration of the deactivated sample

The regeneration of the microencapsulated $LaNi_5$ deactivated by CO was investigated and compared with that of $LaNi_5$. The activated samples were completely deactivated by the repeated CO sorption process. The deactivated samples were evacuated under 10^{-2} Torr for 15 min. The deactivated samples were heated and maintained at regeneration temperatures (423, 523 and 673 K) for 15 min under pure hydrogen pressure of 955 kPa. The samples were evacuated at each temperature for another 15 min, followed by reaction with 955 kPa pure hydrogen at 303 K. The amount of hydrogen absorbed by the samples was measured in terms of the reacted fraction with time until the pressure in the system did not change any more. The samples were again deactivated completely by the repeated CO sorption process and the above procedures were repeated.

Figs. 10 and 11 show the measured reacted fraction vs. the number of regeneration cycles at three different regeneration temperatures. The deactivated samples showed almost no reactivity with hydrogen gas at 303 K and 955 kPa. At the elevated temperatures, however, the reacted fraction for both samples increases sub-

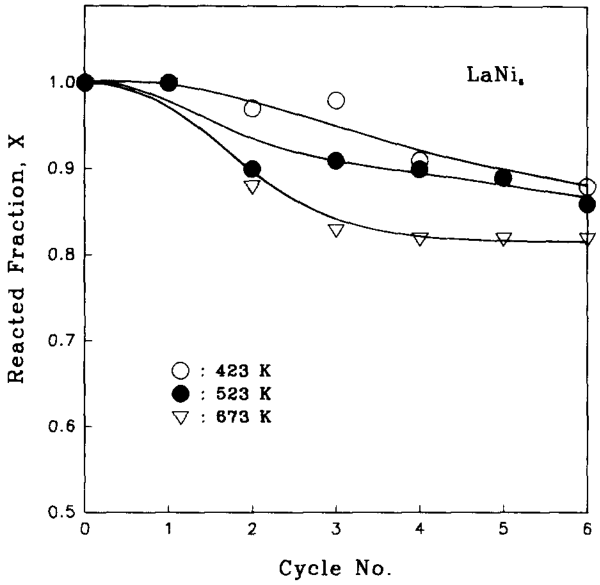

Fig. 10. Plots of reacted fraction vs. regeneration cycle for $LaNi_5$ at 423 K (○), 523 K (●) and 673 K (▽).

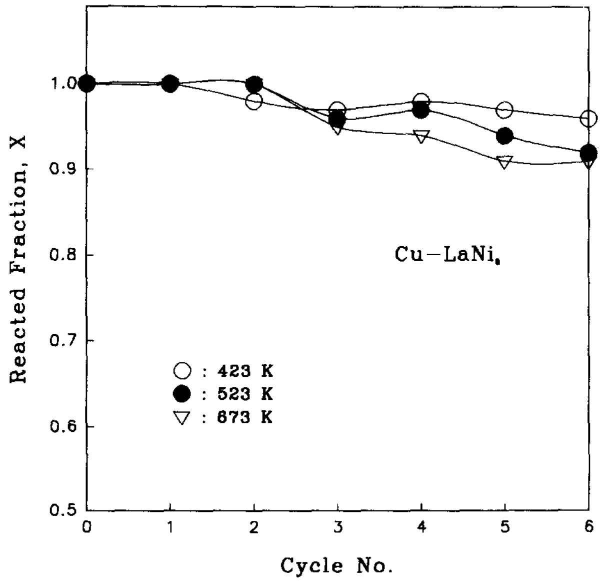

Fig. 11. Plots of reacted fraction vs. regeneration cycle for the microencapsulated $LaNi_5$ at 423 K (○), 523 K (●) and 673 K (▽).

stantially. For $LaNi_5$, the reacted fraction decreases with the number of regeneration cycles and temperature, but is maintained at values of more than 80% (Fig. 10). For the microencapsulated $LaNi_5$ powders, however, the fraction decreases slightly with the number of regeneration cycles at higher temperatures, but remains almost 100% (Fig. 11). The hydrogen absorption capacity of $LaNi_5$ has been reported to be deteriorated by decomposition of $LaNi_5$ into LaH and Ni at elevated temperatures [13,14]. In this experiment, however, it is thought that the difference in the extent of regeneration between $LaNi_5$ and microencapsulated $LaNi_5$ is mainly due to the microencapsulation processes employed.

The regeneration of the deactivated samples is generally explained as follows. Molecular CO gas is adsorbed on metal surface at room temperature and dissociated into C and O on the surface at elevated temperatures. The adsorbed C and O react fast with highly reactive hydrogen atoms liberated from $LaNi_5$ to form methane and water, which then escape from the $LaNi_5$ surface [15,16].

The composition of the gas produced after the regeneration of the deactivated samples at 423 K for 15 min was analyzed with gas chromatography. The existence of CH_4 in the produced gas was confirmed by the gas chromatographic analysis. This result indicates that the microencapsulated $LaNi_5$ can be used as a catalyst for the reaction between CO and H_2.

3.4. *Catalytic activity of the microencapsulated $LaNi_5$*

The catalytic activity of the microencapsulated $LaNi_5$ was investigated for the methanation of CO. The catalyst was activated in the fixed bed continuous flow reactor and then evacuated under 10^{-2} Torr at the reaction temperature. Reactant gas composed of 96% H_2 and 4% CO was introduced into the reactor with the flow rate of 1 sccm and reacted over the catalyst at 523 K and 1 atm. Fig. 12 shows the conversion of CO to CH_4 with reaction time. The catalytic activity is very low for $LaNi_5$, but increases substantially for the microencapsulated $LaNi_5$ with increasing the amount of deposited Cu. The microencapsulated $LaNi_5$ prepared in 100% plating solution shows almost 100% conversion of CO in the range of reaction time considered (6 h). The reason why the microencapsulated $LaNi_5$ shows higher catalytic activity for the CO methanation is that the Cu thin film relieves the deactivation of $LaNi_5$ and then the microencapsulated $LaNi_5$ can absorbed much more atomic hydrogen than $LaNi_5$, resulting in the acceleration of the CO methanation by the liberated hydrogen atoms.

The dehydrogenation of methanol was also carried out over the microencapsulated $LaNi_5$. Argon gas saturated with methanol at 30 °C was introduced into the reactor. Analysis of the gaseous products collected at the outlet of the reactor revealed the presence of hydrogen and CO by the dehydrogenation of methanol. These results indicate that the microencapsulated $LaNi_5$ with Cu can be used as a catalyst for hydrogenation and dehydrogenation.

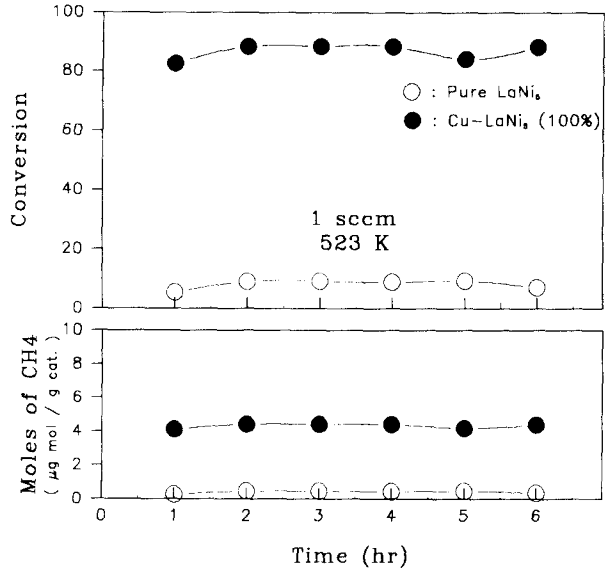

Fig. 12. Comparison of catalytic activities of $LaNi_5$ and microencapsulated $LaNi_5$ with reaction time for methanation of carbon monoxide.

4. Conclusion

A hydrogen storage alloy of $LaNi_5$ was microencapsulated by electroless chemical plating of metallic copper. We investigated the surface morphology of the microencapsulated $LaNi_5$ by varying the plating conditions. The deactivation, regeneration and catalytic activity of $LaNi_5$ before and after the microencapsulation were also studied. $LaNi_5$ was microencapsulated with Cu at temperatures and pH higher than 50 °C and 11 respectively. The weight of Cu deposited increases with the concentration of plating solution. The surface of the microencapsulated $LaNi_5$ powders becomes more smooth with decreasing plating rate. The microencapsulation can greatly inhibit the deactivation of $LaNi_5$ owing to CO. This was thought to be due to the inhibition of contact between CO and $LaNi_5$ surface by the presence of the Cu layer on the $LaNi_5$ surface. The extent of the regeneration of the microencapsulated $LaNi_5$ remained almost 100%, but decreased with the number of regeneration cycles at higher temperatures. For the methanation of carbon monoxide, the catalytic activity of $LaNi_5$ was enhanced greatly by the microencapsulation of $LaNi_5$ with metallic copper.

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