The interaction of alkaline solutions of potassium borohydride with $LaNi_{4.5}M_{0.5}$ (M = Ni, Mn, Cr, Co, Fe, Cu, Al) intermetallic compounds

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The behavior of $LaNi_{4.5}M_{0.5}$ (M = Ni, Mn, Cr, Co, Fe, Cu, Al) intermetallic compounds (IMC) in alkaline solutions of KBH_4 (0.1; 1.0; 4.0 mol L^{-1} KOH) was investigated in the temperature range 298—318 K. The catalytic hydrolysis of KBH_4 is zero order with respect to KBH_4 and first order with respect to IMC. Activation energies of the catalytic hydrolysis of KBH_4 in the presence of IMC are in the range of 60—65 kJ mol^{-1}. The rate of hydrolysis of KBH_4 increases with the concentration of the KOH solution. The hydrogenation of $LaNi_{4.5}M_{0.5}$ in alkaline solutions of KBH_4 yields β-hydride phases for M = Mn, Cr, Co, Cu, Al and α-hydride phases for M = Ni, Fe.

Key words: intermetallic compounds, potassium borohydride, catalytic hydrolysis, reaction order, hydride phases.

The interaction of intermetallic compounds (IMC) that absorb hydrogen with inorganic hydrides, particularly borohydrides of alkaline metals, appears to be one of the possible ways of preparing IMC hydrides without using gaseous hydrogen under high pressure and shows promise as a catalytic process for obtaining hydrogen in the IMC—metal borohydride—solvent system. All the works published to date in this field are concerned with the investigation of the behaviour of IMC in alkaline solutions of $NaBH_4$ only.[1—3]

This work investigates the interaction of the IMC $LaNi_{4.5}M_{0.5}$ (M = Ni, Mn, Cr, Co, Fe, Cu, Al) with alkaline solutions of potassium borohydride. The aim of the work is to study the kinetics of the catalytic hydrolysis of KBH_4 in the presence of the above mentioned IMC as well as to determine the conditions and the composition of the products of IMC hydrogenation in alkaline solutions of KBH_4.

Experimental

To prepare IMC of composition $LaNi_{4.5}M_{0.5}$ (M = Ni, Mn, Cr, Co, Fe, Cu, Al) metals of the following purity (%) were taken: La, 99.79; Ni, 99.99; Cr, 99.7; Cu, 99.99; Fe, 99.96; Mn, 99.8; Co, 99.95; Al, 99.97. A charge was melted in an electric arc furnace with a permanent tungsten electrode on a copper water-cooled hearth in an atmosphere of argon under a pressure of 0.2 MPa. The reguli of the alloys were subjected to 3—4 remeltings and to homogenizing annealing at 873 K for 500 hours followed by hardening in a cold bath. The phase composition of all the prepared alloys was controlled using a DRON-UM-1 X-ray diffractometer. The reguli of the alloys obtained were dispersed mechanically in a ball mill filled with argon before the investigations.

Potassium borohydride was synthesized by the exchange reaction of $NaBH_4$ with KOH in water according to the procedure given in Ref. 4. The purity of KBH_4 obtained was equal to 98.8%.

The investigation of the behavior of IMC in alkaline (0.1; 1.0; 4.0 mol L^{-1} KOH) solutions of KBH_4 was held at temperatures of 298, 308 and 318 K in a temperature-controlled reactor with an accuracy of the reaction mixture temperature of ±0.1 deg. In order to compensate for diffusion restrictions the reaction mixture was stirred intensively by magnetic stirrer.

The processes occurring during the interaction of alkaline solutions of KBH_4 with IMC were monitored by tensimetric-gasometric or the gas-volumetric procedures.

The tensimetric-gasometric procedure was mainly used to investigate the kinetics of the catalytic hydrolysis of KBH_4 in the presence of the IMC $LaNi_{4.5}M_{0.5}$. The amount of hydrogen that formed was checked in an evacuated device of a given volume by means of the pressure registered by a mercury manometer. In this case the amount of hydrogen was calculated based on the known calibrated volume of the device, the measured pressure in the system, and the ambient air temperature.

In addition to the procedures used in our previous investigations[5] the gas-volumetric method was used to study the conditions of IMC hydrogenation reactions in alkaline solutions of KBH_4 and the composition of the reaction products. This made it possible first, to register the gas volume directly in the reaction system and, second, to carry out the reactions at a hydrogen pressure of the system equal to atmospheric pressure, which is necessary for the stabilization of the IMC $LaNi_{4.5}M_{0.5}$ hydride phases resulting from the reaction in alkaline solutions of KBH_4 and having near-atmospheric equilibrium dissociation pressures. In the gas-volumetric system distilled water was used as the working fluid.

Samples were burned in an O_2 stream then the water that formed was absorbed by anhydrous $Mg(ClO_4)_2$ in order to determine the hydrogen content in the α-hydride phases re-

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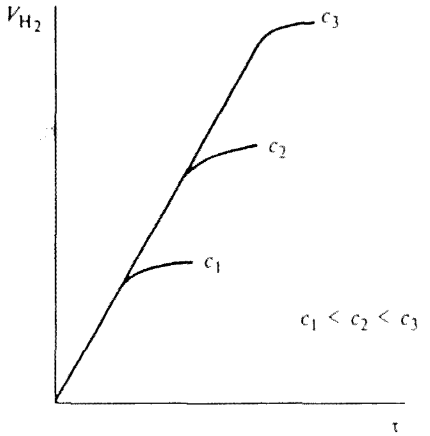

Fig. 1. General view of the kinetic curves of hydrogen release in the hydrolysis of alkaline solutions at different starting KBH_4 concentrations and with a constant amount of $LaNi_{4.5}M_{0.5}$; *c* is KBH_4 concentration, τ is hydrolysis time.

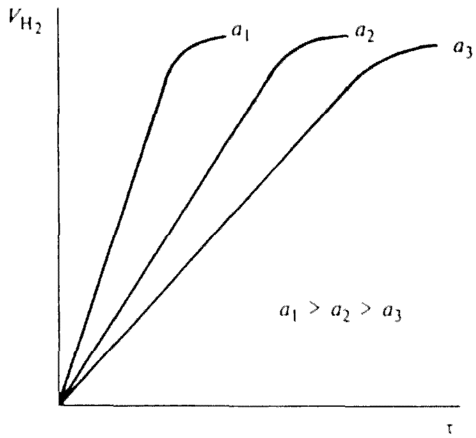

Fig. 2. General view of the kinetic curves of hydrogen release in the hydrolysis of alkaline solutions at constant starting KBH_4 concentration and with different amounts of $LaNi_{4.5}M_{0.5}$; *a* is weighed portion of $LaNi_{4.5}M_{0.5}$.

sulting from the interaction of alkaline solutions of KBH_4 with IMC.

The oxygen content in the IMC samples after the reactions in alkaline solutions of KBH_4 was determined by the method of impulse reduction of the melt in an argon atmosphere.[6]

The specific catalytic activity of IMC in the hydrolysis reaction of KBH_4 alkaline solutions was calculated as the ratio of the KBH_4 hydrolysis constant (k/mol min^{-1}) to the IMC mass (m/g) or to the size of the catalyst surface ($m \cdot S_{sp}$/m^2), where S_{sp} is the specific IMC surface after reaction with the alkaline solution of KBH_4, m^2 g^{-1}.

The specific surface of IMC powders was determined from krypton absorption at the liquid nitrogen temperature and was calculated by the Brunauer—Emmet—Teller method.

Results and Discussion

Studying the catalytic hydrolysis of alkaline solutions of KBH_4 in the presence of IMC $LaNi_{4.5}M_{0.5}$ it was found that the hydrolysis rate increases with the number of hydrolysis cycles for the same sample of IMC. The number of KBH_4 hydrolysis cycles before attainment of the maximum rate of hydrogen formation was in the range of 5 to 15 for the different IMC $LaNi_{4.5}M_{0.5}$. After achieving the maximum rate of hydrogen formation the value of the catalyst specific surface remained constant before and after the next hydrolysis cycle.

IMC $LaNi_{4.5}M_{0.5}$ samples brought to constant characteristics by hydrolysis cycles were used for studying the dependences of the rate of KBH_4 hydrolysis in a 1 *M* KOH solution on the amount of IMC (0.1—1.0 g), the starting KBH_4 concentration (0.05—0.3 mol L^{-1}), and the reaction temperature. The kinetic curves of hydrolysis of alkaline solutions of KBH_4 in the presence of IMC $LaNi_{4.5}M_{0.5}$ (Fig. 1, 2) show that for all the intermetallic compounds investigated the reaction of KBH_4 hydrolysis is zero order with respect to KBH_4 and first order with respect to IMC.

When analyzing the results of the determination of the IMC catalytic activity given in Table 1, the absence of a strictly specified pressure dependency of this activity for the pressure caused by the dissociation of the corresponding IMC hydride phase should be pointed out (Table 2). Nevertheless even the partial replacement of nickel in $LaNi_5$ with other metals can substantially

Table 1. Catalytic activity of $LaNi_{4.5}M_{0.5}$ IMC (M = Ni, Mn, Cr, Co, Fe, Cu, Al) in hydrolysis of KBH_4 (1 *M* KOH, 298 K)

IMC	S_{sp}^{IMC}/m^2 g^{-1} [a]		Specific catalytic activity		Specific catalytic activity $LaNi_{4.5}M_{0.5}$ in $NaBH_4$ hydrolysis[3]
	before the reaction[b]	after the reaction[c]	$k \cdot (m \cdot S_{sp})^{-1} \cdot 10^4$ /mol min^{-1} g^{-1}	$k \cdot (m \cdot S_{sp})^{-1} \cdot 10^4$ /mol min^{-1} g^{-1}	$k \cdot (m \cdot S_{sp})^{-1} \cdot 10^4$ /mol min^{-1} m^{-2}
$LaNi_5$	0.06	1.00	0.75	0.75	0.94
$LaNi_{4.5}Mn_{0.5}$	0.06	0.35	1.10	3.14	5.77
$LaNi_{4.5}Cr_{0.5}$	0.10	0.40	0.75	1.88	3.61
$LaNi_{4.5}Co_{0.5}$	0.05	0.40	0.55	1.38	2.27
$LaNi_{4.5}Al_{0.5}$	0.12	0.75	0.40	0.53	0.64
$LaNi_{4.5}Fe_{0.5}$	0.04	0.70	0.31	0.44	0.57
$LaNi_{4.5}Cu_{0.5}$	0.05	0.82	0.22	0.27	0.24

[a] S_{sp}^{IMC} — specific surface of IMC. [b] After mechanical dispersion in a ball mill. [c] At the maximum rate of hydrogen release.

Table 2. Characteristics of hydride phases of IMC $LaNi_{4.5}M_{0.5}$ (M = Ni, Mn, Cr, Co, Fe, Cu, Al), prepared by interaction with KBH_4 alkaline solutions and by the reaction with gaseous hydrogen under pressure[9]

IMC	Hydrogen content, atom H/mol IMC		p_D/MPa*
	KBH_4 (0.1 MPa)	H_2 (1 MPa)	
$LaNi_5$	0.5	6.0	0.15
$LaNi_{4.5}Mn_{0.5}$	5.3	5.8	0.01
$LaNi_{4.5}Cr_{0.5}$	5.0	6.0	0.04
$LaNi_{4.5}Co_{0.5}$	4.0	6.5	0.1
$LaNi_{4.5}Al_{0.5}$	5.5	5.9	0.015
$LaNi_{4.5}Fe_{0.5}$	1.0	5.6	0.12
$LaNi_{4.5}Cu_{0.5}$	4.0	6.1	0.09

* p_D is pressure caused by dissociation of the hydride phase at 298 K.

Table 3. Dependence of catalytic activity (*k/m*) of $LaNi_{4.5}M_{0.5}$ (M = Ni, Mn, Cr, Co, Fe, Cu, Al) in KBH_4 hydrolysis (298 K) on the concentration of KOH solution

IMC	$(k/m)\cdot10^4$/mol min^{-1} g^{-1} at [KOH]/mol L^{-1}			m_{O_2} (wt.%)[a]	S'_{sp}[b] /m^2 g^{-1}
	0.1	1.0	4.0		
$LaNi_5$	0.45	0.75	1.23	2.82	3.65
$LaNi_{4.5}Mn_{0.5}$	0.57	1.10	2.90	3.15	4.00
$LaNi_{4.5}Cr_{0.5}$	0.40	0.75	0.95	2.60	2.51
$LaNi_{4.5}Co_{0.5}$	0.35	0.55	0.80	2.80	2.25
$LaNi_{4.5}Al_{0.5}$	0.18	0.40	0.95	1.05	1.50
$LaNi_{4.5}Fe_{0.5}$	0.20	0.31	0.50	1.30	0.95
$LaNi_{4.5}Cu_{0.5}$	0.13	0.22	0.43	1.25	0.90

[a] m_{O_2} is oxygen content in IMC after the reaction in 4.0 *M* KOH. [b] S_{sp}' is specific surface of IMC after the reaction in 4.0 *M* KOH.

enhance (Mn, Cr, Co) or diminish (Al, Fe, Cu) the value of the specific surface catalytic activity of IMC. A similar influence of the replacement of the nickel in $LaNi_5$ on the catalytic activity of $LaNi_{4.5}M_{0.5}$ IMC was observed by us previously[3] in studies of the kinetics of the hydrolysis of alkaline solutions of $NaBH_4$. In that case the general trend of the changes in the specific catalytic activity were the same but the absolute values of the specific catalytic activity of IMC $LaNi_{4.5}M_{0.5}$- were lower in the hydrolysis of KBH_4 than in the hydrolysis of $NaBH_4$.

Increasing the temperature of hydrolysis of alkaline (>0.5 mol L^{-1} KOH) KBH_4 solutions even up to 373 K has no noticeable influence on the reaction rate,[7] whereas in the presence of $LaNi_{4.5}M_{0.5}$ IMC this rate increases twofold with a 10 K increase in the temperature (298, 308, 318 K). The apparent activation energies of the catalytic hydrolysis of KBH_4 in the presence of $LaNi_{4.5}M_{0.5}$ IMC calculated on the basis of the experimental temperature dependences of the reaction rate of catalytic hydrolysis are in the interval of 60—65 kJ mol^{-1} which exceeds the analogous values for the catalytic hydrolysis of $NaBH_4$ (50—60 kJ mol^{-1}).[3]

Thus, unlike the homogenous hydrolysis of $NaBH_4$ and KBH_4, noticeable differences between the rates and between the apparent activation energies of the hydrolysis of $NaBH_4$ and KBH_4 in the presence of $LaNi_{4.5}M_{0.5}$ IMC appear. This may be due to the polarizing effect of the cation on the hydrolytic stability of BH_4^-, which starts to appear in catalytic hydrolysis. In order to confirm this hypothesis it would be useful sometime in the future to study the analogous reactions of borohydrides of alkaline metals having larger cations, namely rubidium and cesium.

The effect of the alkalinity of the solution on the catalytic activity of $LaNi_{4.5}M_{0.5}$ IMC in the hydrolysis of $NaBH_4$ studied previously[3] led to an unexpected result that was unknown for metallic catalysts of $NaBH_4$ hydrolysis beforehand. Unlike the catalysts in the form of individual metals: Ni, Co, Fe, Cu, Ru, Pt,[8] for which an increase in solution alkalinity decreases the rate of hydrolysis of $NaBH_4$, for $LaNi_{4.5}M_{0.5}$ (M = Ni, Mn, Cr, Co, Al, Fe, Cu) it was found that an increase in solution alkalinity causes a significant acceleration of $NaBH_4$ hydrolysis that is zero order with respect to $NaBH_4$ and first order with respect to IMC.

According to the results given in Table 3 a similar effect for the hydrolysis of alkaline solutions of KBH_4 is observed. As in the case of $NaBH_4$, the high specific catalytic activity of IMC that appeared after hydrolysis of KBH_4 in a 4.0 *M* solution of KOH remains high in the hydrolysis of KBH_4 in 0.1 and 1.0 *M* solutions of KOH. Taking into account the rather high content of oxygen in the samples of $LaNi_{4.5}M_{0.5}$ and the significant increase in the value of the specific surface of $LaNi_{4.5}M_{0.5}$ after the KBH_4 hydrolysis reaction in 4.0 *M* KOH we may assume that, as for $NaBH_4$, the anomalous increase in the KBH_4 hydrolysis rate in the presence of $LaNi_{4.5}M_{0.5}$ when passing to more concentrated KOH solutions is connected with the irreversible chemical interaction of the surfaces of IMC particles with KOH, resulting in the formation of lanthanum hydroxide and highly catalytically active crystallites of nickel and of the metals replacing it in $LaNi_5$.

The fact that $LaNi_{4.5}M_{0.5}$ (M = Mn, Al) undergo hydrogenation to give hydride phases of composition $LaNi_{4.5}M_{0.5}H_{4.5}$ with equilibrium dissociation pressures of 0.01 and 0.015, correspondingly, was discovered by us earlier[3] while investigating the interaction of $LaNi_{4.5}M_{0.5}$ with alkaline solutions of $NaBH_4$ by the tensimetric-gasometric method. The usage in the present work of the gas-volumetric method, which, unlike the tensimetric-gasometric method, makes it possible to carry out reactions at hydrogen pressures equal to atmospheric pressure enlarged the list of IMC for which the hydrogenation reaction in alkaline solutions of KBH_4 (Table 2), with formation of β-hydride phases containing from 4 to 5.5 hydrogen atoms per 1 mol of IMC for various

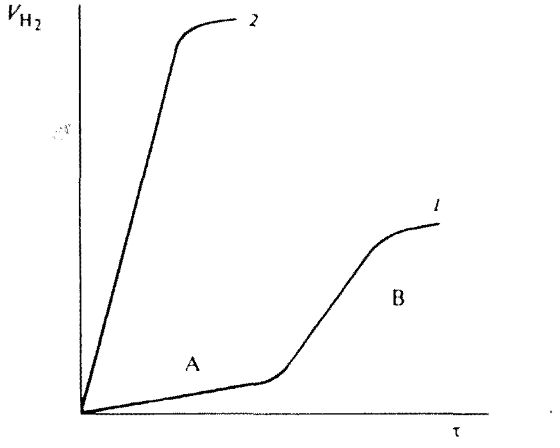

Fig. 3. General view of the kinetic curves of hydrogen release by alkaline solutions of KBH_4 in the presence of $LaNi_{4.5}M_{0.5}$ IMC (M = Mn, Cr, Co, Cu, Al). *1*, first cycle; *2*, second cycle without hydrogen desorption from the hydride phase.

$LaNi_{4.5}M_{0.5}$, was noted. The formation of α-hydride phases containing 0.5 to 1.0 hydrogen atoms per 1 mol of IMC was established from the chemical analysis results for $LaNi_5$ and $LaNi_{4.5}Fe_{0.5}$ IMC, which have hydride phases with equilibrium dissociation pressures exceeding 0.1 MPa.

A general view of the time-dependent hydrogen release curves for the hydrogenation of IMC with the formation of β-hydride phases is shown in Fig. 3. The initial part A of curve *1* is assigned to the main process, the hydrogenation of IMC in the KBH_4 solution, which is accompanied by the release of small amounts of hydrogen during the hydrolysis. On section B the reaction of catalytic hydrolysis prevails, as evidenced by the significant increase in the rate of the release of H_2. The next portion of KBH_4 is catalytically hydrolyzed at the surface of the hydride phase formed (curve *2*) and the initial flattened section A of the gassing curve is absent. The hydrogen in the hydride phase may be desorbed if the temperature increases in the reactor, and then the hydrogenation process may be repeated by adding a new portion of potassium borohydride. The repetition of the hydrogenation and hydrogen desorption cycles results to some extent, as in the case of the reaction of IMC with gaseous hydrogen, in an increase in the hydrogenation rate and a corresponding decrease in the time of the process. However while the interaction of IMC with gaseous hydrogen under pressure in these cycles increases the hydrogenation rate, mainly due to the decrease in sizes of the IMC particles, in the case of borohydride solutions the increase in the catalytic activity of IMC during the hydrolysis reaction of BH_4^- ions that precedes the hydrogenation process plays an important role, in addition to the increased dispersity of IMC.

To obtain the hydride phases of $LaNi_{4.5}M_{0.5}$ by the reaction between IMC and H_2 it is necessary to use pressures in the 0.5—1.0 MPa range[9], whereas interacting IMC with alkaline solutions of KBH_4 and $NaBH_4$[3] does not require such pressures. It seems obvious that, unlike the reaction with gaseous hydrogen, the mechanism of the hydrogenation of IMC in solutions of borohydrides involves the participation of the highly active atomic hydrogen formed at the IMC surface as a result of the reduction-oxidation reaction of the catalytic hydrolysis of BH_4^- ions.

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