Full Articles

Effect of partial substitution of nickel for copper on $LaNi_5$ activation

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The first cycles of hydrogen absorption—desorption in $LaNi_5$—H_2 and $LaNi_{4.5}Cu_{0.5}$—H_2 systems were studied using Tian—Calvet differential heat-conduction microcalorimetry, volumetric measurements, and powder X-ray diffraction. The diffraction profiles were analyzed, and the microstructure characteristics of the $LaNi_5$ and $LaNi_{4.5}Cu_{0.5}$ systems at different stages of activation were determined. The pressure—composition isotherms were plotted, and the enthalpies of phase transitions α→β and β→α were calculated. The effect of substitution on the change in the thermodynamic parameters and microstructure characteristics of the hydride-forming intermetallic compounds during activation was shown.

Key words: intermetallic compounds, hydrides, activation, hysteresis, powder X-ray diffraction, microstrains, calorimetry.

The study of the activation of hydride-forming intermetallic compounds (IMCs) during the first cycles of hydrogen absorption—desorption is important to reveal the mechanism of interaction of hydrogen with the metal matrix. Changes in the rates of hydrogen absorption and desorption, equilibrium pressure in the plateau region, hysteresis and absorption capacity values during the first cycles are related to microstructure transformations in the solid phase.[1] The volume of the crystal lattice of IMC increases by 15—30% upon hydrogenation, due to which the initial intermetallic sample is desintegrated to fine particles (the particle size decreases from 150—300 to 5—25 μm). Simultaneously the size of coherently diffracting domains (crystallites) decreases, the concentration of microstrains increases, and many defects of the crystal lattice (dislocations and vacancies) are formed.[2—5]

The partial substitution of the one of the IMC components for atoms of other elements changes substantially the character of interaction with hydrogen during activation. Since the physical characteristics of metals are non-additive for IMCs formation, it is difficult to predict the influence of a substituting element on the thermodynamic and kinetic parameters of interaction between the compound and hydrogen. The differences observed, namely, the shape of isotherms, hysteresis factor, changes in the dispersion of the samples with an increase in the number

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of cycles, are possibly caused by different characters of distribution of internal strains appeared during hydrogen absorption in the metal matrix. This fact is related[4,5] to a change in the volume effect upon the formation of hydrides of multicomponent IMCs (13—18% for $LaNi_{5-x}M_x$ and 23—25% for $LaNi_5$) and, as a consequence, to a decrease in plastic deformations and the concentration of internal microstrains. It was shown[6—8] that the introduction of a substituent decreases the anisotropy of internal microstrains, and the degree of anisotropy depends on the type of the substituent and its concentration.

Available data do not allow one to reveal a relationship between the microstructure changes and absorption characteristics. Various objects with different degrees of activation were used, as a rule, for studying the microstructure and thermodynamics. Models with different approximations that ignore the influence of some parameters on the diffraction spectrum profile were considered. For instance, the influence of the crystallite sizes on the broadening of the spectral lines was excluded[8,9] completely, which gave overestimated values of the microstrain concentrations. When studying the $LaNi_5$ microstructure, the crystallite sizes were determined by neutron diffraction using the spherical model at the first five activation cycles.[3] The crystallite size was assumed to change isotropically during activation from 2000 Å in the starting sample to 400—500 Å after the first cycle.

In the present work, we used the procedure that takes into account the contributions to the broadening of diffraction lines from both the microstrain value and a change in the size of the coherently diffracting domain (CDD) and calculated these parameters with allowance for the hexogonal crystal lattice of IMCs.

In addition, new fundamental results can be obtained by a procedure of titration of IMCs with hydrogen in a Tian—Calvet differential microcalorimeter. This procedure has several advantages over standard methods for constructing *P—C—T* diagrams. Results of direct calorimetric measurements of the enthalpies of IMC hydrogenation in different regions of the phase diagram depending on the number of cycles make it possible to obtain additional information on the mechanism of activation.

Intermetallic compounds $LaNi_5$ and $LaNi_{4.5}Cu_{0.5}$ were chosen as objects of the study. Unlike such common substituents as manganese, iron, aluminum, and tin, copper can substitute nickel in $LaNi_5$ in any ratio and simultaneously in both crystallographic positions of the structural type of $CaCu_5$: 3g and 2c, while the other substituents occupy the 3g position only.[6,8,10] The atomic radii of Ni and Cu are close (R_{Ni} = 1.24 Å, R_{Cu} = 1.28 Å)[11]; however, these transition metals behave in a different manner toward hydrogen. Therefore, it can be expected that for the identical crystal structure of the whole series of compounds $LaNi_{5-x}Cu_x$ even a minor substitution of nickel for copper would affect the character of incorporation of hydrogen atoms into the metal matrix, the thermodynamic parameters of reaction, and the formation of microstructure at the first absorption—desorption cycles.

Experimental

The initial IMCs $LaNi_5$ and $LaNi_{4.5}Cu_{0.5}$ were prepared by melting of a blend of high-purity metals (La, 99.80%; Ni, 99.96%; Cu, 99.50%) in an electric-arc furnace with a nonconsumable electrode in purified argon. The alloys were remelted 3 times to attain homogeneity. After melting, the samples were weighed to test their correspondence to the specified composition. For all alloys the melting was at most 0.7%. The phase composition of the prepared samples was checked by powder X-ray diffraction.

Hydrogen with the admixture content $\leq 10^{-5}$ vol.% was obtained by desorption from the hydride phase based on the AB_5-type alloy.

The profile analysis of the spectra obtained by powder X-ray diffraction was carried out to determine the crystallite sizes (CDD) and microstrain concentration. Samples for X-ray diffraction studies (before activation and after the first and tenth hydrogenation—dehydrogenation cycles) were thoroughly ground under a hexane layer and studied as suspensions with anhydrous Nujol.

Diffraction patterns were obtained at room temperature on an ARL X′TRA powder diffractometer (Thermo, USA—Switzerland) with the following characteristics: Cu-K(α1+α2) radiation (λ = 1.5406 and 1.5443 Å), reflection mode, angle range 2θ = 18—150°, scanning increment 0.05°, and exposure 2.5 s in each point. Germanium was used as standard to take into account the physical contribution to the line broadening.

To calculate the microstructure parameters, the Outset program for automated X-ray diffraction analysis was used, which was developed on the basis of the Rietveld method at the Moscow Institute of Steel and Alloys.

The calorimetric study of the activation of the $LaNi_5$ and $LaNi_{4.5}Cu_{0.5}$ alloys at 308 K was carried out on an experimental setup consisting of the system of gas dosage and a Tian—Calvet differential calorimeter. Hydrogen was fed to the system in portions with simultaneous detection of the heat release process. The setup and calorimetric titration procedure with hydrogen have been described in detail elsewhere.[12,13]

The hydrogen content in the samples was determined as the H/IMC ratio, *i.e.*, the number of hydrogen atoms per formula unit of the intermetallic compound. Partial molar enthalpies of absorption (desorption) ΔH_p were determined from the heat effect of the reaction

$$\alpha\text{-LaNi}_{5-x}\text{Cu}_x\text{H}_n + m/2\ \text{H}_2 \rightleftarrows \beta\text{-LaNi}_{5-x}\text{Cu}_x\text{H}_{(n+m)},$$

$x = 0, 0.5$.

The error in calculated enthalpy values was expressed through the root-mean-square error of the average result

$$\sigma^2 = \Sigma\Delta^2/n(n-1),$$

where Δ is the deviation of the result from the average one, and *n* is the number of measurements.

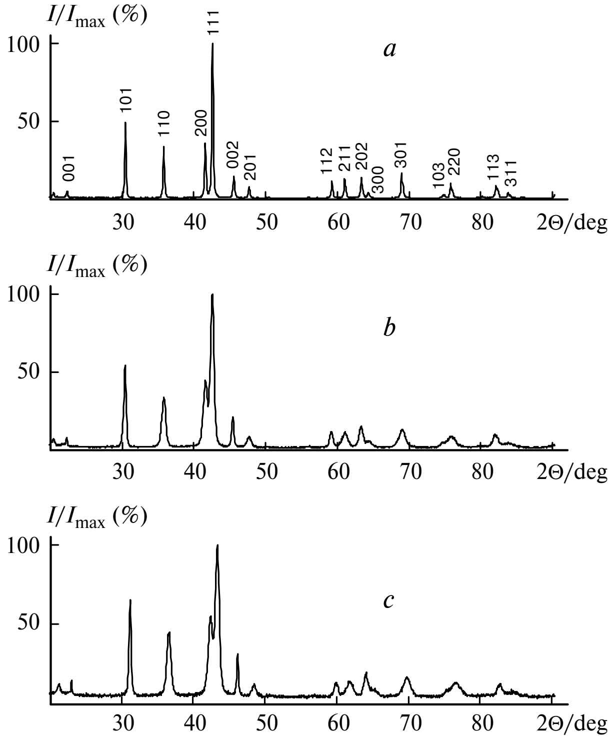

Fig. 1. Diffraction patterns of the initial $LaNi_5$ (*a*) and $LaNi_5$ after the first (*b*) and tenth (*c*) activation cycles.

Results and Discussion

The diffraction patterns of $LaNi_5$ before activation and after the first and tenth hydrogen absorption—desorption cycles are shown in Fig. 1. A substantial difference in the linewidths of the diffraction patterns corresponding to the samples before and after the first activation cycle is seen. The linewidth remains virtually unchanged with the further activation. The diffraction patterns of $LaNi_{4.5}Cu_{0.5}$ are similar.

The results of profile analysis of the diffraction spectra at different activation stages are presented in Table 1. It is seen that after the first cycle of hydrogen absorption—desorption the microstrain concentration (ε) increases considerably, and the anisotropic character of the observed changes is manifested: for the both alloys the ε value along the *a* axis is threefold as large as the ε value along the *c* axis. Since the concentration of internal microstrains in the dehydrogenated samples remains virtually unchanged during further activation, we can speak about the appearance of irreversible deformations. The appearance of many defects in the basal plane agrees with the predominant broadening of lines with *hk*0 indices in the diffraction pattern after the first hydrogenation—dehydrogenation cycle.

In the case of $LaNi_5$, the crystal lattice parameter *a* decreases after the first hydrogenation—dehydrogenation cycle and achieves the initial value to the tenth cycle only. For the copper-substituted alloy, the *a* parameter decreases during the whole activation process, whereas the *c* parameter increases permanently in both cases. This behavior can be explained by the redistribution of metal atoms during hydrogenation to form vacancies.[8,9]

The procedure used by us made it possible to calculate both the microstrain values and CDD sizes with allowance for possible anisotropy. The results obtained (see Table 1) show that the crystallite size of the initial $LaNi_5$ is ~1000 Å and halved after the first cycle in the basal plane only, remaining unchanged along the *c* axis within the determination error. These data give a convincing evidence that the decrease in the crystallite size during activation has a pronounced anisotropic character and, hence, the use of the spherical model[3] is incorrect in this case.

Partial substitution of the nickel atoms in $LaNi_5$ for copper atoms exerts a substantial effect on the microstructure parameters, especially at the first activation cycle. In the copper-substituted alloy, the CDD value along the *c* axis increases twice as large after the first cycle. Although the anisotropy broadening vector remains unchanged (lattice strains appear predominantly in the *hk*0 direction), the concentration of microstrains in both directions is halved compared to that in unsubstituted $LaNi_5$ (see Table 1). The diffraction line broadening in the diffraction pattern of $LaNi_{4.5}Cu_{0.5}$ after the first cycle is less pronounced. Thus, even small copper additives can

Table 1. Microstructure parameters of $LaNi_5$ and $LaNi_{4.5}Cu_{0.5}$ at different activation stages

Sample	Number of cycle	Lattice parameters/Å		Size of crystallites/Å		Concentration of microstrains (%)	
		a	*c*	along axis *a*	along axis *c*	along axis *a*	along axis *c*
$LaNi_5$	0	5.0159(1)	3.9812(1)	1010(20)	1000(30)	0.023(2)	0.010(6)
	1	5.0096(2)	3.9885(2)	530(20)	1100(100)	0.524(4)	0.168(11)
	10	5.0151(3)	3.9957(2)	470(20)	960(50)	0.569(6)	0.120(20)
$LaNi_{4.5}Cu_{0.5}$	0	5.0299(1)	3.9919(1)	1070(20)	890(20)	0.010(5)	0.014(8)
	1	5.0293(1)	3.9922(1)	560(10)	2200(200)	0.204(2)	0.076(5)
	10	5.0256(3)	3.9963(2)	640(30)	1600(200)	0.487(5)	0.085(10)

decrease the number of defects formed upon an increase in the crystal lattice volume during hydrogenation. This effect can be related to two factors: a decrease in the deformation value due to a smaller change in the volume of the $LaNi_{4.5}Cu_{0.5}$ lattice and the influence of substitution on the sensitivity to deformations of the metal matrix itself. Substitution is assumed[8] to prevent the formation of dislocations or to favor their redistribution.

The substitution of even a small nickel amount for copper affects considerably the regularities of alloy destruction during activation. Already after the first cycle the average size of the $LaNi_{4.5}Cu_{0.5}$ particles is 8 μm and further remains unchanged, while the particle size for $LaNi_5$ changes gradually from 25 μm after the second cycle to 5 μm after the fifth cycle.[4,7] The microstructure changes observed during the further activation, *viz.*, a gradual increase in the microstrain concentration and the simultaneous decrease in the crystallite size (see Table 1), occur without changing the particle size.

After the tenth cycle the microstructure parameters of $LaNi_{4.5}Cu_{0.5}$ are comparable with the corresponding values for the unsubstituted compound, which agrees with the published data, according to which the particle size affects the kinetics of hydrogenation only at the first activation stages. It was shown[7,14] that the rate of hydrogen absorption with the $LaNi_{4.9}Cu_{0.1}$ intermetallic compound after the third cycle is by 25 times higher than that for the $LaNi_5$ IMC (desorption proceeds *via* a different mechanism). This specific feature of the copper-substituted alloys can be attributed to the presence of Ni—Cu clusters, whose reactivity toward hydrogen is somewhat higher than that of Ni—Ni clusters, which is used in catalysis.[15]. However, already to the tenth—twentieth cycles when the dispersion, concentration of defects, and elastic strain field in the solid phase of these IMCs become approximately equal, the reaction rate becomes independent of the alloy composition.

The change in the microstructure parameters of the alloys during activation is accompanied by a change in the thermodynamic characteristics of their interaction with hydrogen.

The results of *P—C* measurements at 308 K for the $LaNi_5—H_2$ and $LaNi_{4.5}Cu_{0.5}—H_2$ systems at different activation stages are presented in Fig. 2 and Table 2.

For the both alloys, a higher absorption capacity with respect to hydrogen is observed in the first hydrogenation cycle compared to the subsequent cycles (with a difference of ~0.5 H/IMC). This agrees with the published data,[16] according to which the presence of residual hydrogen in the samples dehydrogenated after the first cycle was confirmed by neutron diffraction. It can be assumed that irreversible anisotropic internal strains that appear during the first absorption—desorption cycle can also be induced by undesorbed hydrogen atoms. Since the cell volume in the dehydrogenated samples does not increase

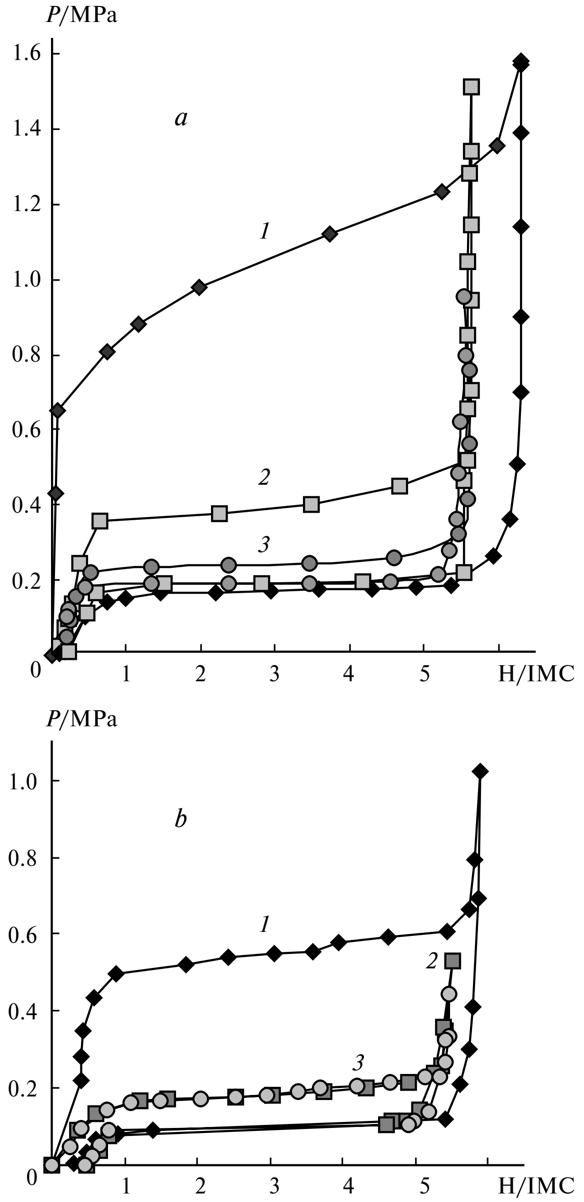

Fig. 2. Pressure—composition isotherms at 308 K for $LaNi_5$ (*a*) and $LaNi_{4.5}Cu_{0.5}$ (*b*): the first (*1*), second (*2*), and tenth (*3*) absorption—desorption cycles.

Table 2. Equilibrium pressures* and the hysteresis factor in the $LaNi_5—H_2$ and $LaNi_{4.5}Cu_{0.5}—H_2$ systems at 308 K

Sample	Cycle	P_{abs}	P_{des}	$RT\ln(P_{abs}/P_{des})$ /kJ (mole of H_2)$^{-1}$
		MPa		
$LaNi_5$	First	1.05	0.17	4.7
	Second	0.38	0.19	1.8
	Tenth	0.24	0.19	0.6
$LaNi_{4.5}Cu_{0.5}$	First	0.54	0.10	4.3
	Second	0.19	0.10	1.8
	Tenth	0.18	0.09	1.6

* For the composition H/IMC = 3.

after the first cycle and even decreases, the hydrogen atoms are concentrated, most likely, on defects. The authors[17] believe that residual hydrogen can act as a surfactant decreasing adhesion between grains, which facilitates the second and subsequent processes of hydrogen absorption.

The decrease in the total absorption capacity upon the partial substitution of the nickel atoms in $LaNi_5$ for copper atoms can be explained by an increase in the number of intersticial sites, whose boundary contains atoms of an element less reactive to hydrogen (Cu instead of Ni), which prevents these interstices to be filled with hydrogen. As shown previously,[6] when 20 at.% nickel are substituted for copper, the number of interstices filled with hydrogen upon hydrogenation in the metal matrix is reduced from five to three.

As can be seen from the data obtained, for all IMCs the equilibrium absorption pressure of the first cycle is much higher than those of the second and tenth cycles. This fact is usually related[2,4] to the necessity of an excess absorption pressure in the first cycle to destroy the sample due to lattice expansion upon hydrogenation and the formation of irreversible defects, for example. dislocations. As shown above, the concentration of strains in $LaNi_{4.5}Cu_{0.5}$ after the first cycle is half as that in $LaNi_5$, and the change in the crystal lattice volume is lower upon hydrogenation. Therefore, it is quite reasonable that the equilibrium absorption pressure of the first cycle decreases after the partial substitution of the Ni atoms in $LaNi_5$ by copper atoms.

The equilibrium desorption pressure remains almost unchanged from the first to tenth cycle. Thus, the hysteresis factor expressed as $RT\ln(P_{abs}/P_{des})$ changes most strongly between the first and second cycles. For $LaNi_{4.5}Cu_{0.5}$ the *P—C* isotherms are reproduced already after the second cycle, whereas for $LaNi_5$ they are reproduced only after the tenth cycle. The size of the $LaNi_5$ particles decreases less intensely than that for $LaNi_{4.5}Cu_{0.5}$, for which the particle size takes the value close to that of the activated state immediately after the first cycle. Therefore, it can be concluded that the achievement of stability of the thermodynamic characteristics during activation depends to a great extent on the rate of sample destruction.

As can be seen from the data in Fig. 2, the activation of $LaNi_5$ results in a noticeable increase in the limiting solubility of hydrogen in the α-phase, while for the copper-substituted compound the extension of the α-region in the phase diagram is independent of the number of cycles. The rate of interaction with hydrogen in the region of an α-solid solution is substantially higher than that in the two-phase region, where the rate is determined by β-phase formation. It can be assumed that the larger the α-region in the isotherm, the higher the rate at the initial hydrogenation stage.

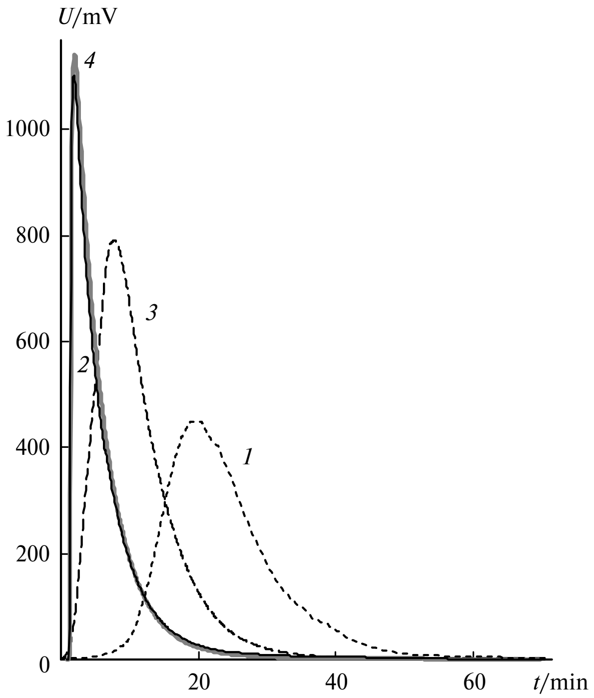

Fig. 3. Heat release curves corresponding to the absorption of the first portion of hydrogen: $LaNi_5$ (first cycle) (*1*), $LaNi_5$ (tenth cycle) (*2*), $LaNi_{4.5}Cu_{0.5}$ (first cycle) (*3*), and $LaNi_{4.5}Cu_{0.5}$ (tenth cycle) (*4*).

This is confirmed by the heat release curves corresponding to the absorption of the first portion of hydrogen (α-region) (Fig. 3). In fact, in the first hydrogen absorption—desorption cycle the hydrogenation rate of the copper-substituted compound is higher than that of $LaNi_5$, whereas to the tenth cycle when the extensions of the α-region in the phase diagrams of the both systems become comparable (see Fig. 2), this difference disappears (see Fig. 3).

The average partial molar enthalpies of the phase transitions α-solid solution $\rightleftarrows$ β-hydride at 308 K were determined from the data of calorimetric measurements.

Sample	$-\Delta H_{\alpha\to\beta}$		$\Delta H_{\beta\to\alpha}$	
	kJ (mole of H_2)$^{-1}$			
	1 cycle	10 cycle	1 cycle	10 cycle
$LaNi_5$	20.3±1.6	32.8±0.5	33.9±0.4	33.0±0.6
$LaNi_{4.5}Cu_{0.5}$	33.8±0.8	33.9±0.7	34.6±0.7	34.5±1.6

The partial molar enthalpy of the phase transition α→β for the first cycle of $LaNi_5$ is lower by the absolute value than those for the subsequent cycles and is characterized by an increased determination error because of the high degree of nonequilibrium of the process (Fig. 4). However, the thermodynamic characteristics of the subsequent hydrogen desorption are already well reproducible. This additionally indicates that the main changes occur during

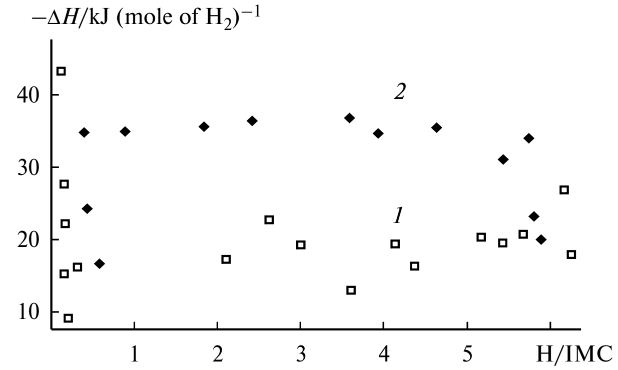

Fig. 4. Differential molar enthalpy of the first hydrogenation as a function of the hydrogen content in $LaNi_5$ (*1*) and $LaNi_{4.5}Cu_{0.5}$ (*2*) at 308 K.

the first hydrogenation of the sample. For the further activation with a decrease in the equilibrium pressure, the enthalpy of the α→β phase transition increases (by the absolute value) and the corresponding parameter of the backward phase transition β→α remains virtually unchanged.

As can be seen from the data in Fig. 4, the introduction of copper as substituent makes the process of the first hydrogen absorption much more equilibrium. The enthalpy of the corresponding α→β phase transition is higher (by the absolute value) than that for $LaNi_5$, which can be related to different energies of hydrogen bonding in cavities of the same type. The differential molar enthalpies of hydrogenation and dehydrogenation of $LaNi_{4.5}Cu_{0.5}$ are unchanged within the determination error beginning from the first cycle (see above).

It can be assumed that the microstructure changes that occur in $LaNi_5$ during the first cycle require additional energy consumption and the process becomes less exothermic. The introduction of a substituent facilitates lattice deformation and decreases the concentration of microstrains appeared during the first absorption. Therefore, in the copper-substituted IMCs the energy consumption decreases and, correspondingly, the difference in enthalpy between the first and subsequent cycles decreases (see above).

The results obtained confirm the relationship between the change in the microstrain concentration and the thermodynamic parameters for both the $LaNi_5$ and copper-substituted IMCs. All considerable changes in the thermodynamic parameters and microstructure characteristics occur in the first activation cycle. The introduction of copper decreases the concentration of anisotropic microstrains and lattice defects appeared in the matrix after the first hydrogenation, due to which the $LaNi_{4.5}Cu_{0.5}$—H_2 system almost immediately demonstrates stable and reproducible thermodynamic parameters, *i.e.*, the sample becomes activated already after the first cycle.

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References

1. N. A. Yakovleva, S. N. Klyamkin, O. A. Veremeeva, and A. A. Tsikhotskaya, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 134 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 135].
2. H. Inui, T. Yamamoto, M. Hirota, and M. Yamaguchi, *J. Alloys Comp.*, 2002, **330—332**, 117.
3. M. P. Pitt, E. Mac A. Gray, and B. A. Hunter, *J. Alloys Comp.*, 2002, **330—332**, 241.
4. J.-M. Joubert, M. Latroche, R. Gerny, A. Percheron-Guegan, and K. Yvon, *J. Alloys Comp.*, 2002, **330—332**, 208.
5. Y. Nakamura, K. Sato, S. Fujitani, K. Nishio, K. Oguro, and I. Uehara, *J. Alloys Comp.*, 1998, **267**, 205.
6. A. Percheron-Guegan, C. Lartigue, and J. C. Achard, *J. Less-Common Met.*, 1985, **109**, 287.
7. L. Belkbir, E. Joly, N. Gerard, T. C. Achard, and A. Percheron-Guegan, *J. Less-Common Met.*, 1980, **73**, 69.
8. Y. Nakamura, K. Oguro, I. Uehara, and E. Akiba, *J. Alloys Comp.*, 2000, **298**, 138.
9. Y. Nakamura, R. C. Bowman, and E. Akiba, *J. Alloys Comp.*, 2004, **373**, 183.
10. M. Latroche, J.-M. Joubert, A. Percheron-Guegan, and P. H. L. Notten, *J. Solid State Chem.*, 1999, **146**, 313.
11. J. Emsley, *The Elements*, Clarendon Press, Oxford, 1991, 256 pp.
12. R. A. Sirotina, A. P. Savchenkova, V. V. Burnasheva, I. F. Belyaeva, and K. N. Semenenko, *Zh. Obshch. Khim.*, 1988, **58**, 2526 [*J. Gen. Chem. USSR*, 1988, **58** (Engl. Transl.)].
13. N. A. Yakovleva, E. A. Ganich, T. N. Rumyantseva, and K. N. Semenenko, *Vestn. Mos. Gos. Univ., Ser. 2. Khim.*, 1995, **36**, 588 [*Vestn. Mosk. Univ., Ser. Khim.*, 1995, **36** (Engl. Transl.)].
14. A. Zarynow, A. J. Goudy, R. G. Schweibenz, and K. R. Clay, *J. Less-Common Met.*, 1991, **172—174**, 1009.
15. I. R. Konenko, E. V. Starodubtseva, Yu. P. Stepanov, E. A. Fedorovskaya, A. A. Slinkin, E. I. Klabunovskii, E. M. Savitskii, V. P. Mordovin, and T. P. Savost´yanova, *Kinet. Katal.*, 1985, **26**, 340 [*Kinet. Catal.*, 1985, **26** (Engl. Transl.)].
16. S. N. Endrzheevskaya, V. S. Luk´yanchikov, A. G. Shablina, V. V. Skorokhod, and E. N. Denbnovetskaya, *Poroshkovaya metallurgiya* [*Powder Metallurgy*], 1984, **9**, 62 (in Russian).
17. K. N. Semenenko, N. A. Yakovleva, and V. V. Burnasheva, *Zh. Obshch. Khim.*, 1994, **64**, 529 [*Russ. J. Gen. Chem.*, 1994, **64** (Engl. Transl.)].

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