

The investigations made in this work made it possible to reveal three basic factors in the positive action on service properties of heat treatment of WC-Co alloys: the change in the amount and sign of the macrostresses in parts of WC-Co sintered carbides; the increase in phase microstresses in the carbide phase; additional solution of W and C in the cobalt. The degree of action of each of these processes on the properties of the alloys cannot be determined since in heat treatment they occur simultaneously. However, in our opinion the change in the sign of the macrostresses in the surface layers of the parts exerts the stronger action on the properties of the alloys.

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#### FEATURES OF THE HYDROGENATION OF TITANIUM- AND MAGNESIUM-BASE

##### COMPOSITE MATERIALS

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Earlier it was shown that regardless of concepts of the necessity of use of high pressures for hydrogenation of magnesium if the magnesium or an alloy of it is in the composition of a pseudoalloy with titanium, impregnation of them with hydrogen is possible under a pressure of 0.1 MPa [1]. The features of the process of hydrogenation of pseudoalloys have been studied in the systems Ti-Mg and Ti-IMV-3 magnesium-lithium alloy. It was established that the degree of hydrogenation of the magnesium constituent depends upon its composition and quantitative content in the pseudoalloy. The hydride of the pseudoalloy Ti-IMV-3 with a volume content of the magnesium-lithium alloy of 25-35% possesses the maximum hydrogen capacity.

The purpose of this work was a more detailed study of the interaction with hydrogen of the titanium-alloy (magnesium-lithium) pseudoalloy and also investigation of the process of hydrogenation of pseudoalloys of titanium with intermetallides of magnesium (Mg-Ni, Mg-Cu, Mg-Y, Mg-La) traditionally used for adsorption of hydrogen [2, 3].

The magnesium compounds were prepared by melting of the components under a layer of flux in steel crucibles with the use of MG95 magnesium, ItM1 yttrium, LaM1 lanthanum, and electrolytic lithium, nickel, and copper (Table 1). Pseudoalloys were produced by impregnation of the sintered porous blanks of PTÉM-2 electrolytic titanium powder with the corresponding molten

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TABLE 1. Composition and Hydrogen Capacity of Magnesium Compounds

Chemical comp., %	Phase comp.	H <sub>2</sub> content, %
85,9 Mg—14,1 Li	β	2,07
70,1 Mg—29,9 Ni	Mg <sub>2</sub> Ni+(α+Mg <sub>2</sub> Ni)	1,08
47,7 Mg—52,3 Ni	Mg <sub>2</sub> Ni+MgNi <sub>2</sub> +(α+Mg <sub>2</sub> Ni)	0,19
40,5 Mg—59,5 Cu	Mg <sub>2</sub> Cu+(α+Mg <sub>2</sub> Cu)	0
54,6 Mg—45,4 Y	Mg <sub>24</sub> Y <sub>5</sub> +Mg <sub>2</sub> Y+(α+Mg <sub>24</sub> Y <sub>5</sub> )	1,17
59,4 Mg—40,6 La	Mg <sub>17</sub> La <sub>2</sub> +Mg <sub>3</sub> La+(α+Mg <sub>17</sub> La <sub>2</sub> )	1,04

TABLE 2. Hydrogen Capacity of the Titanium- and Magnesium-Base Composite Materials

Composition, %	Pseudoalloy		Hydride						
	Volume % of magnesium constituent	Density, 10 <sup>3</sup> kg/m <sup>3</sup>	Calc. weight % of hydrogen	Hydrogenation with a hydrogen pressure of 0.1 MPa				Temp. of the start of liberation of hydrogen, K	Completeness of hydrogenation, % at a pressure of 5-8 MPa
				Temp. of activation and start of hydrogenation, K	Completeness of hydrogenation, %	Density, 10 <sup>3</sup> kg/m <sup>3</sup>	Temp. of the start of liberation of hydrogen, K		
88 Ti—10,3 Mg—1,7 Li	33	3,31	4,53	798	100	2,79	473	93	
82, Ti—12,6 Mg—5,4 Ni	30	3,49	4,25	813	74	2,83	293	—	
79 Ti—10 Mg—11 Ni	26	3,58	3,94	1083	80	2,47	573	80	
80 Ti—8,1 Mg—11,9 Cu	27	3,76	3,83	783	82	3,18	573	—	
82,6 Ti—9,5 Mg—7,9 Y	26	3,50	4,30	903	94	3,27	523	91	
82 Ti—10,7 Mg—7,3 La	30	3,50	4,26	933	95	Crum- bled	573	90	

magnesium-base materials. According to the results of earlier conducted investigations the volume content of magnesium phase in the impregnated pseudoalloys was 26-33%.

The interaction of the pseudoalloys with hydrogen (99.99%) was studied on 30 × 10 × 3 mm specimens. The hydrogenation process was done both under a pressure of 0.1 MPa and at increased hydrogen pressure of 5-8 MPa. In the first case the specimens were activated in vacuum for 0.5 h in the 783-1083°K range. For each composition of pseudoalloy the activation temperature was 0.9T<sub>melt</sub> of the magnesium phase. The hydrogen impregnation was done from an activation temperature up to 273°K with a stepped reduction in temperature by 100°. At each temperature from the start of the sorption process and until reaching the quasiequilibrium state, the hydrogen pressure in the reactor was periodically (each 5 min) measured and returned to the original value (0.1 ± 0.001 MPa), which makes it possible to consider the hydrogenation process as being conducted at constant pressure. The hydrogen content in the specimen was determined from the sum of the drops in pressure in the reactor. With the use of increased hydrogen pressures the activation temperature of the specimens in vacuum was 623°K and of hydrogenation 623-673°K. The hydrogen capacity was determined by high-temperature extraction of hydrogen.

The hydrides were decomposed in heating to 1173°K in vacuum. The temperature of the start of liberation of H<sub>2</sub> was recorded at the moment when the hydrogen pressure above the hydride reached 500 Pa.

The structure of the specimens was studied on a Reichert optical microscope and on a JEM-U3 scanning electron microscope. The specimens were polished with a suspension of chromium oxide in water and etched in an 0.5% solution of nitric acid in alcohol.

The composition of the hydride phases was determined by x-ray diffraction analysis on a DRON-2 diffractometer (CuK<sub>α</sub>, Ni-filter).

The microstructures of the surfaces of the specimens recorded in the characteristic rays of the elements corresponding to the pseudoalloy are shown in Fig. 1. In the Ti-(Mg-Li), Ti-(Mg-Y), and Ti-(Mg-La) composites practically none of the magnesium or alloy elements go into the titanium while in the Ti-(Mg-Ni) and Ti-(Mg-Cu) systems some passage of nickel and copper into the titanium phase occurs.

The sorption capacity for hydrogen of the porous sintered specimens of titanium before impregnation is 410-420 cm<sup>3</sup>/g (activation in vacuum at 1173°K). The hydrogenation of the original magnesium compounds in the form of bars under a pressure of 0.1 MPa occurs at a very low rate, only the surface layer of the specimens reacts with the hydrogen, and the hydrogen capacity reached (Table 1) is an insignificant portion of the theoretically possible.

For all of the investigated compositions of pseudoalloys the hydrogen capacity at low hydrogen pressures is somewhat greater than at higher, which is apparently related to the higher hydrogenation temperature and more complete impregnation of the titanium constituent with a pressure of 0.1 MPa (Table 2). In the case of the Ti-(Mg-Li), Ti-(Mg-Y), and Ti-(Mg-La) pseudoalloys, including all of the components being hydrogenated, the quantity of absorbed

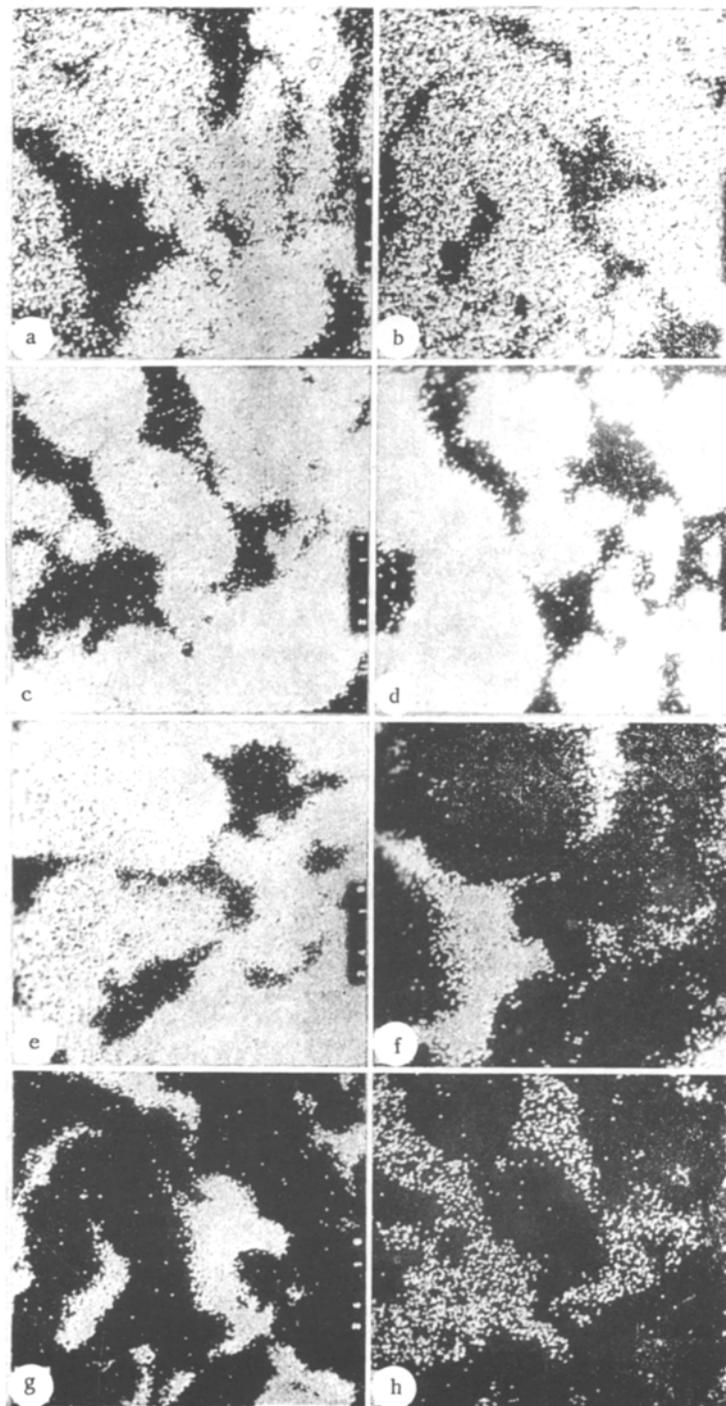


Fig. 1, a-h.

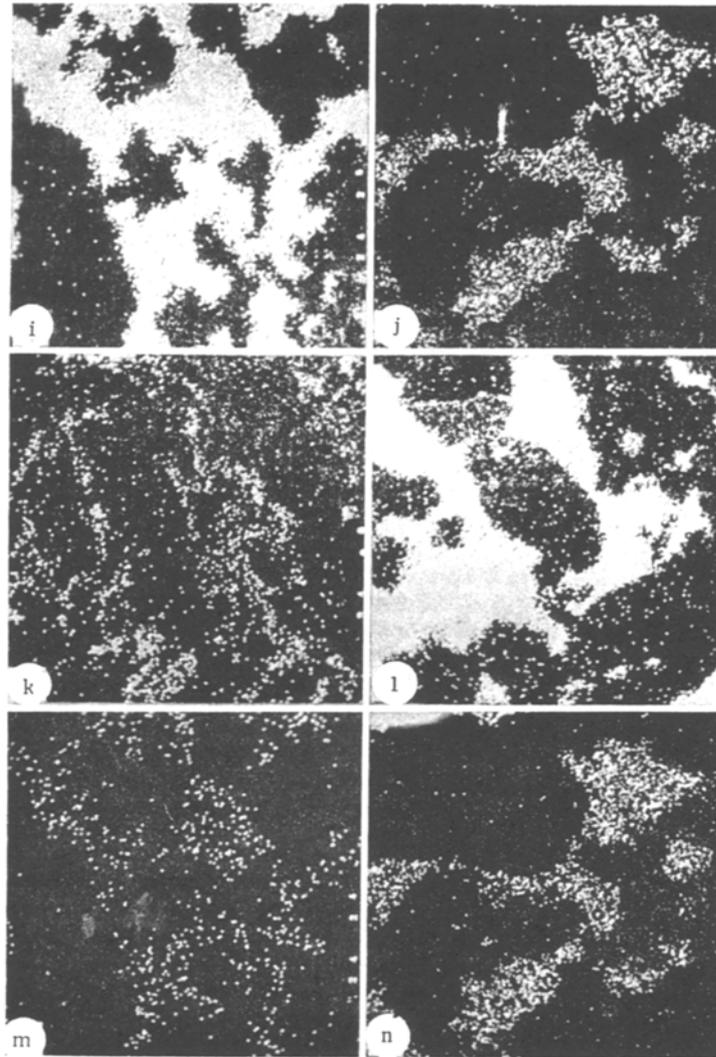


Fig. 1, i-n.

Fig. 1. Surfaces of the specimens of the pseudoalloys in the characteristic rays of titanium (a-e), magnesium (f-j), and the element alloying the magnesium (k-n): a, f) Ti-(Mg-Li); b, g, k) Ti-(Mg-52.3% Ni); c, h, l) Ti-(Mg-Cu); d, i, m) Ti-(Mg-Y); e, j, n) Ti-(Mg-La).

hydrogen per unit of weight is close to the calculated, which corresponds to the total hydrogen content in the stoichiometric binary hydrides of the component metals. The lowest values of hydrogen capacity (substantially below the calculated) are characteristic of the Ti-(Mg-Cu) and Ti-(Mg-Ni) systems.

It may be proposed that incomplete hydrogenation of these two composites occurs as the result of the following factors. The finely dispersed phase of magnesium hydride which is formed in hydrogenation of all intermetallides of magnesium and impurities of pure magnesium phase obtained in insignificant quantities as the result of peritectic decomposition of intermetallides in melting does not form a continuous film and does not prevent diffusion of hydrogen in the pseudoalloy. In contrast to the other compounds the investigated compositions Mg-Cu and Mg-Ni in accordance with the phase diagram contain significant quantities of the pure magnesium-base phase (5-15%). In the first moments of sorption of hydrogen on the surface of the magnesium particles a continuous film of magnesium hydride is formed. As the result of its very low permeability (the diffusion coefficient of hydrogen through magnesium hydride, according to [4], is  $2.5 \cdot 10^{-9}$  cm<sup>2</sup>/sec) access of hydrogen to the intermetallide phases

and titanium is difficult, which leads to incomplete hydrogenation of the composites. Apparently there are no obstacles in principle to complete hydrogenation of the pseudoalloys Ti-(Mg-Cu) and Ti-(Mg-Ni). To avoid the formation of continuous films of magnesium hydride it is necessary to control the structure and chemical composition of the magnesium constituent.

In the products of hydrogenation of all of the pseudoalloys x-ray diffraction analysis records two phases of titanium hydride of the same composition,  $TiH_{1.92}$  with cubic ( $a = 0.445$  nm) and tetragonal ( $a = 0.447$ ,  $c = 0.44$  nm) lattices, and magnesium hydride  $MgH_2$ . On x-ray diffraction patterns of the composites Ti-(Mg-Y), Ti-(Mg-La), and Ti-(Mg-Ni) after hydrogenation lines corresponding to the phases  $YH_2$ ,  $LaH_3$ , and  $Mg_2NiH_4$ , respectively, were observed.

After hydrogenation the Ti-(Mg-Y) and Ti-(Mg-La) specimens crumble under an insignificant force while the specimens of all of the other compositions are covered with cracks but preserve their form and are not broken by hand. As the result of hydrogenation the volume of the specimens increases by 21-26% with preservation of their form.

The temperature of active decomposition in vacuum of the hydrides of all of the investigated pseudoalloys is relatively high. A feature of decomposition of the hydrides of Ti-(Mg-Li) and Ti-(Mg-Ni) (nickel content in the magnesium constituent 29.9%) is two-step liberation of hydrogen. The Ti-(Mg-Li) hydride starts to dehydrogenate at 473°K and liberates about 4% of the total adsorbed hydrogen. In the 773-1173°K range the quantity of liberated hydrogen is 66% of the adsorbed. In the Ti-(Mg-Ni) hydride dehydrogenation starts at 293°K, 2.7% of the  $H_2$  is liberated in the 293-723°K range, and then the quantity of dehydrogenated hydrogen increases sharply and at 773°K reaches 20.5% and at 1173°K 75.3% of the adsorbed hydrogen. The character of decomposition of the hydrides of the other pseudoalloys is practically the same; upon reaching the temperature of the start of decomposition (Table 2) active liberation of hydrogen is observed.

An analysis of the thermodynamic rules of the process of hydrogenation of magnesium and its compounds shows that in principle complete impregnation of them under a hydrogen pressure of 0.1 MPa is possible. However, methods of hydrogenation known until now have not made it possible to accomplish this process in connection with the presence on the surface of the magnesium of oxide films and the very low diffusion rate of hydrogen through the magnesium hydride formed. The investigations conducted make it possible to conclude that in the composition of the pseudoalloys (in this case with titanium) not only magnesium alloys but also intermetallics of magnesium are almost completely impregnated with hydrogen under a pressure of 0.1 MPa. The proposed pseudoalloys may be recommended as high-temperature carriers and sensors of hydrogen.

The study of the kinetics of hydrogenation makes it possible to decide upon in more detail the features of the mechanism of adsorption of hydrogen by individual pseudoalloys.

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