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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Resistance to Hydrogen of Al–Sc Alloys

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Abstract—The behavior of aluminum–scandium alloys in hydrogen at an equilibrium pressure of 0.1 MPa was studied on a Sieverts apparatus.

The most efficient modifier of aluminum is scandium [1]. Addition of 1% Sc to AV000 aluminum yields the maximal number of grains (1090 per 1 cm^2) compared to other modifiers. Aluminum and aluminum alloys modified with scandium have the improved strength, plasticity, corrosion resistance, and other operation characteristics [2]. Scandium-doped aluminum has found application as structural material for aircrafts. Electrodes made of aluminum wire doped with 1% Sc facilitate welding of aluminum parts [3, 4], which allows fabrication of compact light articles. However, the strength of these materials, when operating for a long time under conditions of sharp temperature gradients, depends on their resistance to the environment in which they are exploited, in particular, air and hydrogen plasma.

In this work we studied the hydrogen absorption capacity of Al–Sc alloys. As known, compact aluminum does not interact with hydrogen. Aluminum hydride (AlH_3) as a white amorphous mass can be prepared solely by the chemical method from the ether solution [5]. Scandium absorbs hydrogen in the elemental state, forming the hydride ScH_2 [6], and also as a component of intermetallic compounds with metals that are not hydrogenated. For example, the intermetallic compound $ScMn_2$ yields hydrides $ScMn_2H_{3.8}$ [7]; $ScFe_2$, $ScFe_2H_4$; and $ScCo_2$, $ScCo_2H_4$ [8].

In the Al–Sc system, four intermetallic compounds are formed: Al_3Sc, Al_2Sc, AlSc, and $AlSc_2$ [9, 10]. The solubility of Al in Sc reaches about 6.25%. The limiting solubility of Al in Sc is 0.30%. At high crystallization rates the solubility of Sc can reach 5.1%. The data on the crystal structure of the phases in the Al–Sc system are given in Table 1. The crystal structures and the unit cell parameters of aluminum and the nearest intermetallic Al_3Sc are close. Therefore, as was shown by practical experience, cracks resulting from internal stresses do not appear in aluminum alloys containing up to 30% Sc at their various mechanical and thermal treatments. The behavior of these alloys in hydrogen-containing media was not studied previously.

EXPERIMENTAL

The alloys under study were obtained from aluminum (A999 ultrapure grade) and SkM-2 grade scandium containing (wt %) 99.88 Sc, 9×10^{-3} Fe, less than 0.001 Cu, 0.0051 Al, 0.05 Ca, 0.02 Mg, less than 0.001 Y, less than 0.0005 Yb, less than 0.005 Zr, less than 0.005 Ti, and 0.016 Si. The starting materials were smelted in an electric arc furnace with a permanent tungsten electrode under purified argon. Each sample was melted sixfold. The content of the elements in the alloys was determined by X-ray fluorescence analysis on a VRA-30 device. In some tests, chemical analysis was also used.

The alloys were hydrogenated at a 0.1 MPa hydrogen pressure on the improved quartz apparatus of the Sieverts type [6]. The volume of the reaction chamber was 60 cm^3. The pressure was measured with a mercury manometer. The hydrogen uptake was monitored by the pressure change in the system. The pressure was adjusted to the initial value every 5 min. Hydrogen was obtained by decomposing titanium hydride or $LaNi_5$ hydride in a reactor connected to the reaction chamber. Owing to plasticity, aluminum alloys containing up to 2% Sc were used as powder, which was prepared from finely disperse cuttings washed with ethyl alcohol and sieved. The other alloys were used as crushed ingots. Metallic scandium was hydrogenated without crushing.

We measured the sorption isobars at 0.1 MPa hydrogen pressure. Before hydrogenation, the alloys were activated by heating to 600–800°C at 13 Pa.

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Table 1. Crystal structure of phases in the Al–Sc system [9, 11]

Phase	Prototype	Pearson's symbol	Space group	Structure designation	Lattice parameters, nm		
					a	*b*	*c*
Al	Cu	cF4	*Fm*3*m*	Al	0.4041	–	–
Al_3Sc	$AuCu_3$	cF4	*Pm*3*m*	Ll_2	0.4105	–	–
Al_2Sc	Cu_2Mg	cF24	*Fd*3*m*	Cl5	0.758	–	–
AlSc	CsCl	cP2	*Pm*3*m*	B2	0.5030	0.9895	0.3126
$AlSc_2$	$InNi_2$	hP6	$P6_3/mmc$	$B8_2$	0.488	–	0.6166
β-Sc	Cu	cI2	*Fm*3*m*	A2	0.454	–	–
α-Sc	Mg	hP2	$P6_3/mmc$	A3	0.3309	–	0.5273

Table 2. Sorption characteristics of scandium–aluminum solid solutions after activation at 600°C for 1 h

Sample	H_2 content, $cm^3\ g^{-1}$, at indicated temperature, °C							H_2 content in alloy, %
	600	500	400	300	200	100	20	
Al + 0.3% Sc:								
compact	0	1.4	2.0	4.3	5.3	7.1	8.9	0.08
powder	1.1	1.3	18.1	18.5	24.2	27.5	39.3	0.35
Al + 2% Sc:								
compact	0.4	2.0	3.5	4.0	7.1	13.1	13.9	0.14
powder	6.0	6.0	7.5	10.9	15.0	25.1	58.8	0.52

After activation, hydrogen was fed into the reactor, where the sample preheated to the maximal temperature was located, and the hydrogen sorption was observed and recorded at constant temperature till the saturation was complete. After that, the temperature was decreased by 100°C. The sorption process was resumed till the saturation was observed at the given temperature. The test was performed at stepwise decrease in the temperature to room temperature. The incubation period was observed in none of the cases. The total time of the experiment reached 3–5 days.

We found that all the compositions studied are hydrogenated reversibly and after decomposition in a vacuum and subsequent hydrogenation the final content of hydrogen in them is similar to the results of the first hydrogenation. The exception was metallic scandium. In the course of the first hydrogenation it took up only 86.6 cm^3 of H_2 per 1 g and disintegrated by cracking. No hydrogen was released in a vacuum at 900°C, and only at 1000°C it started decomposing. The results of the second hydrogenation are given in Table 2. Heating it in a vacuum was accompanied by intense cracking, indicative of transformation of the hydride structure. It can be presumed that, as in the Ti–H system [12, 13], hydrogen shifts the temperature of the β-Sc → α-Sc transition toward lower temperatures (the temperature of the α-Sc → β-Sc transition in air is 1337°C). In this case, as in the majority of studies, no scandium hydride of the composition ScH_2 was obtained. The hydrogen content in the hydride obtained corresponds to the composition $ScH_{1.39}$.

The hydrogen content in solid solution and scandium–aluminum alloys depends on dispersity (Table 2). Hydrogen absorption is stronger for powders owing to developed surface. On heating Al + 0.3% Sc and Al + 2% Sc samples to 600°C in a vacuum, about 7–10 cm^3 of adsorbed hydrogen per gram of the alloy is released, with most of hydrogen remaining in the alloy lattice. Concerning the effect of hydrogen on aluminum alloys, Dobatkin *et al*. [14] report that "...hydrogen content exceeding 0.2 cm^3 per 100 g drastically deteriorates impermeability of ingots. Also, it can affect impermeability of deformed semifinished products. Unfortunately, study of this effect, which is so important for estimating the potential of metals in spacecrafts, is given little attention yet."

The data on hydrogenation of the intermetallic compounds are given in Table 3. Before interaction with hydrogen, the alloys were activated in a vacuum

Table 3. Data on hydrogenation of intermetallic compounds of the Al–Sc system and scandium after the first cycle of hydrogenation–dehydrogenation

Sample	Activation		P_{H_2}, MPa	H_2 content, $cm^3\ g^{-1}$, at indicated temperature, °C									H_2, %**
	T, °C	τ, h		800	700	600	500	400	300	200	100	20	
Al_3Sc	600	1.0	0.1	–	–	0	2.5	24.5	24.5	25.6	42.5	44.6	0.40
Al_2Sc	900	0.7	0.1	7.6	14.3	17.7	25.5	32.5	38.4	41.4	69.5	75.6	0.67
AlSc	900	0.5	0.1	20.7	32.2	41.1	50.9	66.7	72.1	75.5	86.5	98.0	0.87
$AlSc_2$	800	0.5	0.1	104.0	105.9	106.6	107.1	126.9	129.4	131.4	150.2	189.5	1.15
$AlSc_2$*	200	0.5	2.5	–	–	–	–	–	–	–	10.0	241.9	2.16
Sc	900	0.5	0.1	320.9	321.0	321.0	321.0	322.0	326.0	327.0	338.0	338.0	3.0

* After the third cycle.
** Maximal H_2 content at 20°C.

at 800–900°C. The exception was Al_3Sc, which was activated at 600°C to prevent possible partial peritectic decomposition at 660°C. The maximum amount of hydrogen absorbed by $AlSc_2$ was smaller compared to similar AB_2 alloys (e.g., $NiMg_2$ and $NiTi_2$: 404 and 298 $cm^3\ g^{-1}$, respectively). As known [15], the solubility of hydrogen in aluminum and scandium and the diffusion rate of hydrogen in these metals grow with increasing pressure. It is presumed that the hydrogen pressure of 0.1 MPa is insufficient for complete saturation of $AlSc_2$. Therefore, the intermetallic compounds were hydrogenated at 2.5 MPa in a stainless steel installation. Additional activation of the alloy grains was performed by repeated hydrogenation–dehydrogenation cycles without removing the sample from the reaction chamber (Table 3).

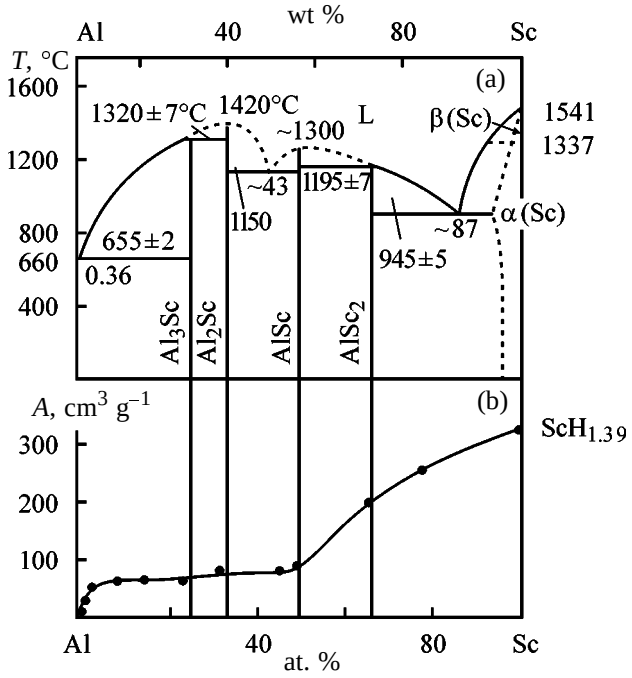

Fig. 1. (a) Phase diagram of the Al–Sc system and (b) maximal sorption capacity for hydrogen of the system alloys vs. alloy composition. (*T*) temperature and (*A*) sorption capacity at P = 0.1 MPa and 20°C.

We studied the influence of activation temperature and number of activation cycles on hydrogenation. After the third cycle the amount of sorbed hydrogen reached 241.9 cm^3 H_2 per gram of the alloy. Only minor amount of hydrogen (9.9 cm^3 H_2 per gram) was revealed by chemical analysis of the material hydrogenated at 200°C and 2.5 MPa. Thus, the hydride of $AlSc_2$ is extremely unstable, instantaneously decomposing at room temperature as the hydrogen pressure is quickly relieved from 2.5 to 0.1 MPa. For its storage the special stabilization procedures are necessary. Many hydrides, including $LaNi_5$ hydride, behave similarly. To stabilize them, the surface is saturated with oxygen or carbon dioxide at the temperature of liquid nitrogen.

The sorption capacity for hydrogen as a function of composition of the Al–Sc system is plotted in Fig. 1. All alloys of the system, especially intermetallic compounds, absorb hydrogen. If during fabrication of scandium-doped aluminum, namely, in the stage when aluminum–scandium charge is introduced into aluminum melt, the homogenization of the melt was not attained and scandium segregated in the course of subsequent crystallization, then, for example, in spacecraft articles and liquid-hydrogen cylinders, especially on warming them from the sun side, Al_3ScH_x or Al_2ScH_x can be formed with high probability. Scandium can segregate into intermetallic compounds in the course of rolling ingot and during welding with a scandium-containing wire owing to crystallization of a weld material. The resulting hydrides decompose with hydrogen evolution, resulting in the formation

of pores during diffusion. The hydrogen accumulation in a spacecraft in the presence of oxygen can cause explosion and fire.

In this work, the influence of the other components of traditional aluminum alloys, for example, magnesium and lithium alloys, on their resistance to molecular hydrogen was not studied. Presumably, the presence of these elements easily forming hydrides MgH_2 and LiH would deteriorate the hydrogen resistance of aluminum–scandium alloys.

CONCLUSION

(1) All alloys of the Al–Sc system interact with hydrogen. The intermetallic compounds Al_3Sc, Al_2Sc, AlSc, and $AlSc_2$ form hydrides.

(2) The amount of sorbed hydrogen grows with increasing hydrogen pressure.

(3) The $AlSc_2$-based alloy can be used for preparing hydrogen-accumulating materials.

(4) The aluminum alloys containing scandium can be recommended for aerospace technology only after testing them for hydrogen resistance.

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