NASA TECHNICAL MEMORANDUM

NASA TM-75360

HYDROGEN ABSORPTION IN SOLID ALUMINUM DURING
HIGH-TEMPERATURE STEAM OXIDATION

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JAN 1979
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546   JANUARY 1979

1. Report No. NASA TM-75360	2. Government Accession No.	3. Recipient's Catalog No.		
4. Title and Subtitle HYDROGEN ABSORPTION IN SOLID ALUMINUM DURING HIGH-TEMPERATURE STEAM OXIDATION		5. Report Date Jan. 1979		
		6. Performing Organization Code		
7. Author(s) L.A. Andreev, B.G. Gel'man, A.A. Zhukhovitskiy (Moscow Institute of Steel & Alloys)		8. Performing Organization Report No.		
		10. Work Unit No.		
9. Performing Organization Name and Address Leo Kanner Associates, Redwood City, CA 94063		11. Contract or Grant No. NASW-3199		
		13. Type of Report and Period Covered Translation		
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, DC 20546				
		14. Sponsoring Agency Code		

15. Supplementary Notes

Translation of "Pogloshchenie Vodorova Tverdym Alyuminiem pri Vysokotemperaturnom Okislenii v Parakh Vody," Fiziko-khimicheskie Issledovaniya Metallurgicheskikh Protsessov, Vol. 1, 1973, pp. 90 - 94.

16. Abstract

Hydrogen is emitted by aluminum heated in a vacuum after high-temperature steam treatment. Wire samples are tested for this effect, showing dependence on surface area. Two different mechanisms of absorption are inferred, and reactions deduced.

17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified-unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22. Price

HYDROGEN ABSORPTION IN SOLID ALUMINUM DURING HIGH-TEMPERATURE STEAM OXIDATION

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During vacuum heating after high-temperature steam treatment, <u>/90</u>* samples of aluminum release significant amounts of hydrogen. The greater part of this emitted hydrogen consists of the so-called "surface" hydrogen. The process of emission of "surface" hydrogen during vacuum heating is still little studied. In particular, there is a lack of data characterizing the kinetic development of this process, which among other things is extremely important to the study of the oxidation of metals in aqueous steam.

The process of metal oxidation and the growth of a protective oxide layer is not limited to the external "oxide-gas" boundary. It also proceeds, although to a much smaller extent, at the "metal-oxide" boundary. When metal is oxidized in steam, this process can cause the hydrogenation of the metal, since the hydrogen released by the oxidation beneath an oxide layer at the "oxide-metal" interface may dissolve into the metal.

This paper studies the absorption and emission of different fractions of hydrogen after steam treatment of hydrogen. It considers the dependence of these processes on the properties of the oxide layer and external conditions.

Method of Investigation

The experiment used cylindrical aluminum samples of equivalent volume, 0.8 and 0.2 mm in diameter and 200 and 3200 mm long,

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respectively, of type AB000. The samples were cleaned and then soaked for 3 minutes in a 10% NaOH solution, followed by 3 minutes in a 10% HNO_3 solution. After three hours of preliminary heating at 600°C in a vacuum, the quartz tube containing the samples was cut off from the vacuum pumps, and the samples were subjected to isothermal steam heating. At the end of the steam heating, the system was pumped out again, during which time the samples were placed in an oven. In this way the condensation of the steam onto the oxide layer was avoided. Finally, the samples were drawn from the oven and allowed to cool.

The decomposition of the steam at the cathode of the omegatron gauge led to the formation of hydrogen. To eliminate this side effect which introduced an uncontrollable error into the analysis of the samples, we mounted two liquid nitrogen traps in front of the RMO-45 gauge. These completely absorbed the steam, even at momentary emissions 100 times greater than occurred during the annealing of the samples.

During analysis the samples were inserted in turn into the oven and heated to the temperature necessary to extract the gas. Any water vapor was caught by the traps, while the emitted hydrogen was continuously pumped through the omegatron gauge. The total amount of emitted hydrogen was the area under the curve drawn by the automatically recording pen [1].

Interaction of Steam and Aluminum

We determined the amount of hydrogen emitted by samples of aluminum wire during vacuum heating after their exposure to steam at 200, 400, 500, and 600°C for different periods of time. In all cases when the duration of steam exposure was increased above 30 minutes, the amount of hydrogen reached a certain limiting value and was subsequently unchanged. Table 1 presents these characteristic limiting values for a steam partial pressure

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TABLE 1.

HYDROGEN CONTENT, IN CM^3/100 G,
EMITTED BY ALUMINUM SAMPLES DURING VACUUM
HEATING AFTER 30 MINUTES' EXPOSURE
TO STEAM AT 18 MM HG

Surface area, cm^2	Steam temperature, °C			
	200	400	500	600
5	0.08	0.07	0.09	0.05
20	0.05	0.05	0.09	0.05

of 18 mm Hg. It follows from the table that the amount of hydrogen emitted after exposure to steam at 200 and 400°C is perhaps 1.5 times greater from the samples of wire with the smaller area (when dia. = 0..8 mm, σ = 5 cm^2) than from the samples of larger surface area (when dia. = 0.2 mm, σ = 20 cm^2). On the other hand, the amount of hydrogen emitted after exposure to steam at 500 and 60.0°C is the same for samples of different surface area.

This circumstance prompts the hypothesis of different types of hydrogen retention by aluminum interacting with water vapor. It also points out the essential difference in the characteristic parameters of the emission of hydrogen from samples after steam treatment at these two ranges of temperature. Since the diffusion coefficient of hydrogen in aluminum in the range 200–400°C is extremely small, it is natural to assume that the accumulation of hydrogen during interaction with water proceeds mainly as a result of a process of adsorption (which is possible in the form of an OH$^-$ group). At higher temperatures, the actual absorption of hydrogen by the metallic samples becomes possible. Thus, the mechanism of its emission during the subsequent heating in a vacuum will be different.

The characteristic parameters of the kinetics of hydrogen emission during vacuum heating were determined from the curves of gas emission recorded by the automatic pen. The curve measuring the partial pressure of hydrogen gas during the heating typically contains a maximum; it represents the result of two processes, the emission of gas at the rate I and the pumping out

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of gas at the speed S. Thus,

$$VdP = Idt - SPdt,$$ (1)

where P is the partial pressure of hydrogen in the system;

V is the volume of the system.

After integrating (1) and assuming that I declines exponentially with time, we use the linear relation between the signal of the omegatron gauge, h, and the partial pressure of hydrogen, P = mh, to obtain:

$$h = \frac{C_0 k}{mV(A-k)} [\exp(-kt) - \exp(-At)],$$ (2)

where C_0 is the initial concentration of hydrogen in the sample;

k is the gas emission constant;

A ≡ S/V is the pumping constant.

The experimental curves were treated in accordance with equation (2). The values of the constants k and A were obtained from the straight line formed by the experimental curve h = h(t) in the co-ordinates

$$h - [\exp(-kt) - \exp(-At)].$$

The calibration value of the pumping constant A was determined by a preliminary experiment [1]. The error in k determined by this method does not exceed 20%. The values of the constant obtained in this manner are incorporated in Table 2.

Table 2 indicates that the coefficient k of samples subjected to steam treatment at 200-400°C depends neither on the geometric surface area of the sample nor on the duration of the steam treatment (at least, in the interval 1-300 minutes). The energy of activation of hydrogen emission, which is obtained from the temperature dependence of k, is about 21,000 cal/mole after 30 minutes' exposure to 400°C steam at 18 mm Hg. On the other

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hand, in the temperature range 500-600°C, the rate of hydrogen emission during subsequent vacuum heating depends substantially on the sample surface area and the length of exposure to the steam. The ratio of the coefficients of gas emission for samples of different surface area, $k_{\sigma=20}/k_{\sigma=5}$, is 3 to 3.5.

The hyrogen absorption during steam treatment depends on the means used to prepare the sample. In particular, with a complete surface treatment (etching + vacuum heating), absorbed hydrogen is observed in both temperature ranges only in thin wire samples (dia. of 0.2 and 0.8 mm), while thicker (4 mm dia.) samples, also cold drawn, do not display this effect.

TABLE 2.

DEPENDENCE OF THE RATE CONSTANT $k(\text{min})^{-1}$ OF HYDROGEN EMISSION ON THE TEMPERATURE AND DURATION OF STEAM TREATMENT AT 18 MM HG (VACUUM HEATING AT 600°C)

Steam temp., °C	Surface area, cm²	Exposure time, minutes					
		2	5	30	180	300	420
200	5	—	0.8	0.8	—	—	—
	20	—	0.8	0.8			
400	5	—	0.8	0.70	—	0.70	—
	20	—	0.8	0.80	—	0.80	—
500	5	0.37	—	0.30	0.20	—	0.10
	20	1.20	—	1.00	0.70	—	0.35
600	5	0.35	—	0.15	0.10	0.10	0.10
	20	1.00	—	0.50	0.35	0.35	0.35

Obviously, the crystallographic nature of the oxide layer on aluminum does not depend on the diameter of the wire; consequently, the observed effect is related to a certain type of inhomogeneity in the structure of the surface. In the contrary case, that is, assuming samples with homogeneous surfaces, we would expect an effect to be observed in every trial.

The three types of aluminum samples, naturally, differ in the extent of preliminary baking and structural peculiarities. The thin samples were obtained by means of prolonged baking, and they were characterized by a "bamboo" structure. The thick samples (4 mm in dia.) were polycrystalline in structure. It is quite natural to relate the observed phenomenon of hydrogen

absorption by aluminum with the special structural feature of the surface, the edges of the bamboo sections, which during the prolonged baking cause the recrystallization of the material in the stage of cold deformation. On these sections, which are distinguished by an elevated corrosion activity, it is possible for the corrosion products to accumulate, creating a surface for development and an adsorption capacity. On the other hand, the oxide layer is essentially disturbed near these section edges, which reduces their resistance to further oxidation, and this is probably the fundamental source of the volume hydrogenation of the metal. This process can be expressed as the total reaction

$$2Al + {}^3/_2 H_2O = Al_2O_3 + 3[H].$$
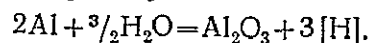
As the dependence of the coefficient k on the sample surface area indicates, however, the entire surface takes part in the emission of hydrogen during vacuum heating. The process possibly involves a limited amount of penetration by hydrogen across the oxide layer to the metal.

As a result of special surface treatment (in this case, steam treatment at 600°C and 10 mm Hg for one hour), the thick cylindrical samples also acquired an absorption capacity for hydrogen during high-temperature steam oxidation. We obtained the effect, to be specific, as a result of boiling the samples in distilled water for 4 hours and heating them in a vacuum for 3 hours at 600°C. The experimental results were as follows:

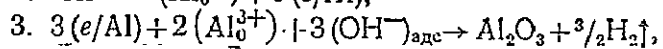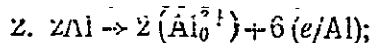| Sample weight, g:	0,250	0,420	0,480	0,800	1,480
Hydrogen, cm³/100 g:	0,062	0,061	0,063	0,062	0,057

The proportional increase in the amount of hydrogen emitted, during vacuum heating at increasing sample weights, is evidence of volume absorption of the hydrogen by the mass of aluminum.

Just as in the case of the samples of thin wire, we observe
local sections on the surface of the massive samples boiled
in water which, upon subsequent high-temperature steam treatment,
developed intensive oxidation of the metal and simultaneous
volume hydrogenation.

The generation of "surface" hydrogen upon the vacuum heating
of samples after preliminary steam treatment at comparatively
low (400°C) temperatures is probably caused by OH⁻ groups which
are strongly absorbed on the aluminum oxide in local sections
of the surface of the samples. The treatment of the oxidized
samples with steam creates a layer of absorbed ions, thus:

$$1. \ 3H_2 + 3\,(e/Al) \rightarrow 3\,(OH^-)_{адс} + {}^3/_2 H_2 \uparrow.$$
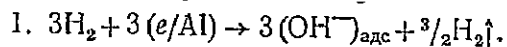
During the subsequent vacuum heating, the following reactions
take place:

$$2. \ 2Al \rightarrow 2\left(Al_0^{3+}\right) + 6\,(e/Al);$$
$$3. \ 3\,(e/Al) + 2\left(Al_0^{3+}\right) + 3\,(OH^-)_{адс} \rightarrow Al_2O_3 + {}^3/_2 H_2 \uparrow,$$

where (e/Al) are electrons in the conducting band of the metal;
$(Al_0{}^{3+})$ are cations between lattice nodes (internodal).

We must realize that the slowest stage of the oxidation of
Al is reaction 2, the process of dissolving cations into the
internodal layers of oxide [2]. This process must be assisted
by an electrostatic polarity, created as a result of the adsorp-
tion of negatively-charged particles on the exterior surface at
the "oxide-gas" interface. If E is the electric field strength,
n_0 the number of ions per cm² of the surface of the metal, D the
diffusion coefficient of the ions, then the cation current
across the oxide layer, according to [2], is equal to:

$$j = D_0 n_0 \frac{eE}{kT}. \tag{3}$$

Since in this case the oxidation proceeds due to an adsorbed
layer, to that extent, the process of depositing OH⁻ groups on /94

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the surface will slow down. Consequently, at $E = \dfrac{4\pi e n_{OH^-}}{\varkappa \xi^2}$

(where ξ is the thickness of the oxide layer;

n_{OH^-} is the concentration of hydroxide ions on the surface;

$\varkappa$ is the dielectric constant of the oxide);

then

$$j = \frac{4\pi e^2 D_0 n_0}{kT\varkappa}\left(\frac{n_{OH^-}^0 - {}^3/_2 \int\limits_0^t j\,dt}{\xi}\right). \tag{4}$$

The final expression for j, after the integration of (4), is

$$j = j_0 e^{-\frac{6\pi e^2 D_0 n_0}{\varkappa kT \xi}}. \tag{5}$$

In this case, the gas emission constant, k, is essentially independent of the sample surface area. There is an approximate correspondence of the activation energy of the process (21,000 cal/mole) with that calculated earlier from the data on the kinetics of oxidation [2]. This supports the assumptions made concerning the limited extent of emission of hydrogen during vacuum heating.

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2. Grimli, T., "Oxidation of metals," in: Khimiya Tverdogo Sostoyaniya ("Solid State Chemistry"), Moscow, IIL, 1961, p. 479.