THE EFFECT OF A SURFACE OXIDE LAYER ON THE RATE OF HYDROGEN EMISSION FROM ALUMINUM AND ITS ALLOYS IN HIGH VACUA

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ABSTRACT

This article reports experimental results of hydrogen emission from samples of hydrogen etched with 10% NaOH. A derived equation of the rate of hydrogenation during etching is shown to agree satisfactorily with the results of experiment.
EFFECT OF SURFACE OXIDE FILMS ON THE RATE OF HYDROGEN EVOLUTION FROM ALUMINUM AND ITS ALLOYS IN A HIGH VACUUM

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This article considers the effect of an oxide layer on the surface of aluminum and the alloys AMg and AMts on the kinetics of the emission of hydrogen at high vacua and temperatures.


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We have studied the influence of surface oxide layers on the rate of hydrogen emission at the high vacuum of $10^{-8}$ torr at temperatures from 20 to 450°C, using pure ABOO aluminum, the cast alloy AMg, and cast and deformed samples of the alloy AMts.

It is well known that aluminum and its alloys form thin films of the oxide $\text{Al}_2\text{O}_3$, the removal of which is difficult and hardly sensible, since upon exposure to the atmosphere the oxide is formed anew. It is therefore appropriate to consider the effect of the surface oxide layer and its thickness on the rate of hydrogen emission from aluminum and aluminum alloys at a high vacuum.

The rate of oxidation of aluminum is determined by the rate of formation of internodal cations at the surface of the metal and the rate of the diffusion of the cations across the oxide layer, forming oxide molecules at the "oxide-gas" interface. At room temperature the oxidation of aluminum practically ceases an hour after beginning. The determination of the actual layer thickness is difficult in this case, but it does not, apparently, exceed 10-20 Å. At higher temperatures (up to 400-500°C), the growth of the oxide layer varies parabolically with time, which is explained by the action of the well-known Cabreri-Mott mechanism.

* Numbers in the margin indicate pagination in the foreign text.
In the present work we did not specifically measure the thickness of the oxide layer on aluminum and aluminum alloys as a function of the temperature and the time of exposure, so the values of the thickness of the oxide layer under different conditions were evaluated according to results given in the literature.

Samples of the investigated materials measuring 60 x 40 x 3 mm, cleaned to the same surface purity, were tested after appropriate cleansing for gas separation at a high vacuum. The high-vacuum testing chamber, 0.5 l in volume, was connected to a high-vacuum electromagnetic pump across a special diaphragm. Such an intermediate diaphragm creates a return pressure between the test chamber and the high-vacuum pump, giving a directional flow to the gas from the tested samples to the pump (the stream method).

Pressure gauges and omegatron mass-spectrometer lamps were soldered onto the walls of the test chamber right beside the samples, so that we obtained a qualitative as well as quantitative analysis of the gases emitted from the sample material [1, 2]. The alloy AMg was tested at high vacuum after 10 minutes' oxidation at 20°C and 180 minutes at 500°C. See Figure 1.

The experiment shows that an artificially accelerated growth of the oxide layer by means of three hours' exposure to air at 500°C does not essentially change the hydrogen emission from AMg at high vacuum. This occurs, probably, because the oxide layer artificially induced at 500°C is basically composed of magnesium oxide formed at the surface of the alloy, since magnesium ions diffuse through the initial oxide layer more rapidly than aluminum ions.
The artificial oxide layer produced in this manner is also less dense than aluminum oxide and does not display its protective properties.

We also studied the effect of the thickness of surface oxide layers on the rate of hydrogen emission at high vacua from cast and deformed samples of AMts alloy. The deformed AMts samples were prepared by strong compression on casts heated to 450-500°C, resulting in samples with especially thin profiles (3-5 mm).

Preliminary testing showed that the flattening of the grains of the AMts alloy as a result of plastic deformation had no noticeable effect on the rate of hydrogen emission at high vacua. This regularity is maintained even after surface oxidation of the alloy, at the same oxide thickness for deformed and undeformed samples.

Let us examine the effect of thickness of the oxide layer on rate of hydrogen emission by AMts alloy at high vacua. If we assume that oxidation of AMts proceeds at the same rate as oxidation of pure aluminum, then, following the results given in the scholarly literature, exposure of the alloy to air for 10 minutes at 20°C creates an oxide layer approximately 10 Å thick, while 10 minutes at 500°C, approximately 100 Å, and 180 minutes at 500°C, approximately 600 Å.
Experimental results indicate that the increase of the thickness of the surface oxide layer of the AMts alloy from 10 to 100 Å decreases the rate of hydrogen emission at high vacua and temperature substantially. See Figure 2.

Figure 2 shows that the hydrogen emission from a 10 Å oxide layer from 20 to 200°C consists of $(1.3 - 1.5) \times 10^{-10}$ torr·cm²/sec, $4.3 \times 10^{-10}$ torr·cm²/sec at 250°C, and $1.3 \times 10^{-9}$ torr·cm²/sec at 300°C. A 100 Å oxide layer has corresponding emission levels of $(5.1 - 4.3) \times 10^{-11}$, $1.2 \times 10^{-10}$, and $2.3 \times 10^{-10}$ torr·cm²/sec. An increase in the oxide layer from 100 Å to 600 Å does not create an observable further decrease in the rate of hydrogen emission.

Such an effect of the surface oxide layer of the rate of hydrogen emission in a high vacuum is related to energy states, since the wide disparity between the dimensions of hydrogen protons and the oxide lattice parameter excludes any possible connection between the geometry of the crystalline lattice and the rate of hydrogen diffusion.

According to the theory of oxidation, the formation of a compact (without any pores) oxide layer occurs as a result of
the meeting of migrations of aluminum ions and oxygen ions inside the layer under the influence of an electric field.

The fundamental feature of this theory, which is also significant for the diffusion of hydrogen, is the representation of motion of ions in the oxide layer. It assumes that the boundary of the oxide layer is essentially a potential barrier limiting the entry of metal and oxygen ions into the layer. As a result, the positive aluminum ions accumulate at the "metal-oxide" interface, and the negative oxygen ions pile up at the "oxide-gas" interface.

Since hydrogen diffuses in its ionized state as a proton, neither the accumulation of aluminum cations nor the potential barrier at the boundary of the oxide layer nor the electric field within it can prevent the diffusion of the hydrogen protons from the metal across the oxide layer into the vacuum. As the thickness of the oxide layer increases, the strength of the electric field inside the layer declines and reduces the barrier properties of the layer. One can then understand why a 600 Å oxide layer on AMts alloy has less protective properties than a 100 Å layer.

Figure 2 shows that for a given thickness of surface oxide layer, ABOO aluminum has the slowest rate of hydrogen emission at high vacuum. The low rate of hydrogen emission from pure aluminum can be explained by the lesser degree of hydrogen saturation in aluminum compared to its alloys, as well as the better protective properties of its oxide.

Thus, an experiment to examine the effect of the surface oxide layer on the rate of hydrogen emission in high vacua from aluminum and its alloys shows that an oxide layer on the AMg alloy does not possess the capacity to hinder the diffusion of hydrogen.
The artificial oxidation of the AMts alloy by exposure to air for 10 minutes at 500°C substantially decreases the hydrogen emission rate in high vacuum to approximately the rate from oxidized pure aluminum.

Thermodynamic calculations of the reactions of the generation and dissociation of aluminum oxide show that degasification at high temperatures (up to 600°C) and vacua will not reduce the thickness of artificially-generated surface oxide layers on aluminum and its alloys. This makes it possible to use the artificial oxidation of aluminum and certain of its alloys as a method of reducing their rates of hydrogen emission under conditions of high and ultra-high vacuum.
REFERENCES
