Oxygen-Induced Segregation of Hydrogen on a Magnesium Surface Observed by Time-of-Flight Analysis of Direct Recoils

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Time-of-flight analysis of direct atomic recoils produced by pulsed Ar^+-ion irradiation of a polycrystalline magnesium surface enables the identification of hydrogen, as well as other surface atoms. The data demonstrate the direct detection of surface hydrogen and the first direct observation of oxygen-induced surface segregation of hydrogen in a metal at room temperature.

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Chemisorption of gases on alloy surfaces may cause profound changes both in surface structure (geometry) and in surface composition.[1] The latter effect arises from the enhancement in the exchange between surface and bulk atoms of one of the alloy constituents leading to a change in surface composition. There are examples of such chemisorption-induced segregation for different adsorbate-alloy combinations.[1] Some recent works on this effect have been done on hydride-forming alloys such as $LaNi_5$,[2,3] Mg_2Ni,[4] FeTi,[3,5] and Ti_2Ni-type compounds.[5] In these systems, oxygen-induced surface segregation of the more active constituent in the alloy occurs, enriching the surface with the oxidized form of this species. Some of the hydrogenation properties of such intermetallic compounds have been accounted for by these oxygen-induced surface segregation effects.[2-5] Adsorption-enhanced segregation of impurities, such as carbon and sulfur, in various metals is also documented.[1]

Hydrogen is known to exist as one of the main impurities in metals and alloys, forming either alloy-type hydrogen solid solutions or hydride precipitates. In principle, surface segregation effects and chemisorption-induced segregation effects of hydrogen impurities are expected to take place. However, since the direct detection of surface hydrogen is not possible by most of the conventional surface analysis techniques, the adsorption-induced surface segregation of hydrogen is difficult to observe. In this Letter we report the direct observation of oxygen-induced surface segregation of hydrogen; the effect is demonstrated on a polycrystalline magnesium surface.

We observe the surface hydrogen as well as other surface species using a procedure suggested by Chen *et al.*[6] and later confirmed on a hydrogen-contaminated Cu surface[7] and on radiation-damaged CsBr.[8] In this procedure an ion beam and detector are positioned to create and detect forward scattered and sputtered particles as shown in the inset in Fig. 1. A surface atom of mass M_R struck by a primary ion of energy E_I and mass M_I recoils with an energy given by

$$E_R = E_I[4M_IM_R/(M_R+M_I)^2]\cos^2\varphi,$$

where φ is the recoil angle measured in the laboratory frame (see Fig. 1). Hydrogen (or any other surface atom) recoiled toward the detector will arrive at the detector at a time of flight (TOF) calculable from E_R, if not scattered or blocked by another surface atom. If the kinetic energy of the recoiled hydrogen exceeds about 100 eV, it can be detected by a Channeltron particle multiplier in either a neutral or an ionized state. We have measured the ion fraction of hy-

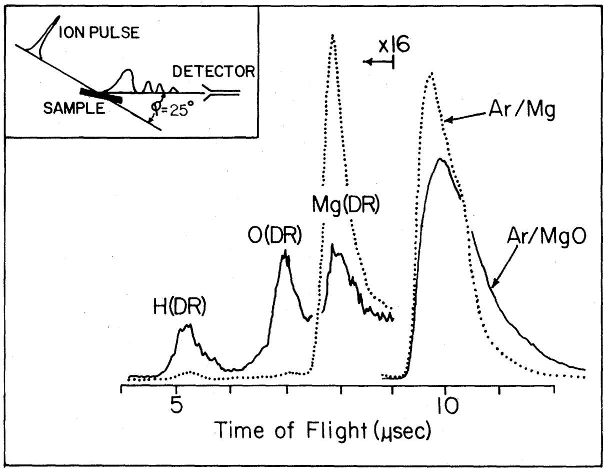

FIG. 1. Time-of-flight spectra of direct recoils from polycrystalline magnesium. Dotted line, sputter-cleaned surface; full line, after 10-L O_2 exposure (5×10^{-7} Torr × 20 sec). The direct-recoil (DR) peaks of the different surface atoms are indicated in the figure. The inset illustrates the experimental arrangement of the incident ion pulse and detector.

drogen directly recoiled from a magnesium surface, and, since it is less than 2%, the ability to detect neutrals is crucial to the experiment. The same argument applies for any other surface atom present along with the hydrogen so that by careful choice of E_I, M_I and φ, a TOF spectrum resolving all recoiled surface atom peaks can be obtained. The intensities of the recoil peaks are determined by the sensitivity of the Channeltron multiplier to the different atoms, by the collision cross section of each surface atom, and by their concentration and specific surface geometry.

For the present analysis we applied a pulsed beam of 3-keV Ar^+ ions on a polycrystalline magnesium surface at an incidence angle of about 15° from the surface plane. The detector was placed at a 25° forward scattering angle, which is lower than the critical angle for single scattering of Ar from a Mg atom (37.5°) but higher than the critical angle for scattering from an O atom (23.6°). Figure 1 presents the corresponding TOF spectra obtained for sputter-cleaned and for oxygen-saturated Mg surfaces. Each spectrum was obtained within 2 min after either Ar^+ cleaning or oxygen exposure. Reactions with residual gases will be shown to be insignificant under these experimental conditions. The intensity of the scattered argon peak is about an order of magnitude greater than the peaks of the recoiled surface atoms. In the present case, the total area of the Ar scattering peak remains almost constant upon oxygen adsorption, though its shape and width vary significantly. The area of this peak is thus usable as an indirect measure of the primary ion flux. The areas of the direct-recoil peaks were normalized to the area of the Ar scattering peak, and are plotted in Fig. 2 as a function of oxygen exposure determined by uncorrected ionization gauge readings [in langmuirs (L), 1 L = 10^{-6} Torr sec]. Each point in this figure was obtained by exposing the sample to the given dose, then pumping and taking the recoil measurement. It is seen that surface concentrations of hydrogen, oxygen, and magnesium follow a saturation-type behavior. For the oxygen and magnesium, the slopes of these exposure curves decrease to a small value at approximately 2-L O_2 which agrees well with previously reported observations of the adsorption of oxygen on the magnesium surface.[9-11]

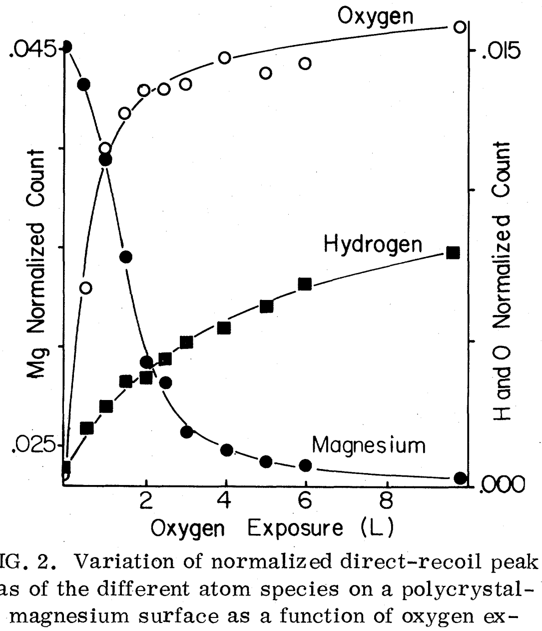

FIG. 2. Variation of normalized direct-recoil peak areas of the different atom species on a polycrystalline magnesium surface as a function of oxygen exposure (in langmuirs) at room temperature (see text).

The striking feature in Figs. 1 and 2 is the pronounced increase in the surface concentration of hydrogen concurrent with the oxygen exposures. This hydrogen must come either from a reaction with residual gas-phase H_2 and water or from the magnesium bulk (i.e., oxygen-induced surface segregation of hydrogen). We now show that the rate of accumulation of surface hydrogen due to the residual-gas-phase reaction is insignificant during the experiment.

The surface concentrations of hydrogen on the sputter-cleaned surface as a function of exposures to either H_2 or H_2O were obtained in a manner analogous to that used in determining the oxygen data presented in Fig. 2. The hydrogen surface concentrations were then similarly determined on a surface first exposed to 20-L O_2 and then to successive exposures to either water or hydrogen. A complete description of these experiments will be presented elsewhere; however, the pertinent conclusions are summarized as follows. (i) The values of the various *initial* slopes in the plots of the normalized hydrogen peak areas versus gas dose are listed in Table I. (ii) When the sputter-cleaned magnesium is exposed only to O_2 the resulting surface hydrogen-to-oxygen signal ratio obtained at saturation is nearly 25% of the hydrogen-to-oxygen signal ratio resulting from the total reaction of a cleaned surface with water. (iii) Also it is observed that the accumulation rates of hydrogen for both H_2 and H_2O are much faster on the oxidized surface than on the clean metal surface; furthermore, the reaction rate of water is much faster than that of gaseous hydrogen. Therefore, if the

TABLE I. Rates of accumulation of surface hydrogen (normalized recoil H counts per langmuir) due to various gas-phase reactions with a clean and an oxidized magnesium surface.

Surface	Reacting gas H_2	 H_2O
Clean Mg	3.2×10^{-5}	3.7×10^{-4}
Oxidized Mg (20-L O_2 exposure)	5.0×10^{-4}	1.1×10^{-2}

source of the oxygen-induced accumulation of hydrogen were a gas-phase-contaminant reaction, then the most significant contribution would be from the reaction of residual water with the oxidized magnesium surface.

An *in situ* mass spectrometer (RGA) was used to measure the composition of the residual gases and monitor contaminants introduced during the O_2 dosing. We found a factor of about 2–3 increase in the water level during the 20-sec oxygen dosing. The oxygen and water concentrations returned to the base levels of the residual gases within 20 sec after closing of the oxygen leak valve. Assuming a partial pressure of water of 6×10^{-10} Torr and using the reaction rate given by Table I (for the oxidized magnesium surface), we can calculate the expected increase in the hydrogen surface concentration during a 10-L O_2 exposure (20 sec $\times 5\times10^{-7}$ Torr O_2) due to the gas-phase (water) reaction. The result obtained in this manner is less than 2% of the observed increase in the hydrogen surface concentration, indicating the insignificant contribution from gas-phase reactions. In order to confirm this estimate experimentally, and to exclude the possibility that the freshly formed oxide reacts with the water at a rate which is much faster than that given in Table I, we exposed a clean magnesium surface to a mixture of O_2 and water. The partial pressure of O_2 was 5×10^{-7} Torr (as in the pure oxygen exposures) and that of water was 1×10^{-8} Torr (which is higher by a factor of about 20 than the estimated partial pressure of water during a pure oxygen exposure). The hydrogen concentration obtained after a 20-sec exposure of this mixture (corresponding to 10-L O_2) was less than 2% larger than that obtained during a 10-L pure oxygen exposure, indicating the insignificant contribution of the water reaction during the data acquisition.

It is thus concluded that oxygen-induced segregation of hydrogen occurs on the magnesium surface. To obtain an estimation of the hydrogen impurity level in magnesium necessary for such a segregation process to occur, we must first estimate the surface hydrogen coverage. As mentioned before, when the sputter-cleaned magnesium is exposed to the saturation level of oxygen the resulting surface hydrogen-to-oxygen peak ratio is nearly 25% of the hydrogen-to-oxygen peak ratio resulting from a totally water-reacted surface which we assume to be almost completely hydroxylated. Also, a simplified calculation[12] based on inverse power differential collisional cross sections predicts a hydrogen-to-oxygen peak intensity ratio of about 1.6 for a fully hydroxylated surface, while the experimentally observed ratio obtained from Fig. 2 (at 10-L O_2) is about 30% of this value. If we assume 1.2×10^{15} oxygen atoms/cm^2 on the MgO surface, the concentration of the segregated surface H atoms (at 10-L O_2 exposure) is about 4×10^{14} H atoms/cm^2. The room-temperature diffusion coefficient of hydrogen in magnesium (α phase) is 3.5×10^{-9} cm^2/sec.[13] It is difficult to estimate accurately the diffusion time required for the completion of the segregation process. However, this time should be shorter than the 2 min needed for the completion of the recoil measurement. Choosing arbitrarily a diffusion time of 1 min implies a diffusion path of about 4.6 μm, and a corresponding minimum bulk concentration of hydrogen of about 20 ppm. This value is well below the hydrogen contamination level[14] in magnesium and assures the feasibility of the presently observed segregation process.

Adsorption-induced segregation processes[1] are usually controlled either thermodynamically (i.e., by the tendency of the system to reach its most stable state) or kinetically (i.e., by the mobility of the different constituents). It is expected, thus, that at low temperatures, when the diffusion rate of hydrogen becomes very low, this segregation effect will vanish. Indirect evidence in the literature seems to confirm this expectation.

An x-ray photoemission spectroscopy study of the adsorption of oxygen on a Mg(0001) single-crystal surface has been reported by Ghijsen *et al.*[10] At room temperature, two distinct O 1*s* peaks are observed during the adsorption process at low binding energy (LBE) of 530.0–530.9 eV and at high binding energy (HBE) of 533.0–533.1 eV. The LBE peak corresponds to an "oxidic" type of oxygen (in MgO) and the HBE peak is similar to a "hydroxidic" type of oxygen [in

$Mg(OH)_2$]. The authors of Ref. 10, however, preferred to assign the HBE peak to the presence of an "incomplete" distorted oxide form, though they did not exclude the possibility of a hydroxidic form. Our results clearly suggest that a "hydroxidic" form could appear on the Mg surface during the room-temperature oxygen exposure, which would account for the HBE peak.

The appearance of such a HBE additional peak is mentioned also in the work of Fuggle[11] for oxygen adsorption on polycrystalline magnesium, where the author notes that for experiments at 300 K a shoulder on the HBE side of the O 1*s* peak was stronger than at 100 K. Since we assign this HBE shoulder to the oxygen-induced H segregation, this observation is consistent with the expected low-temperature kinetic limit of the hydrogen surface segregation.

The extension of the present room-temperature study to a larger temperature range and to other metals is anticipated.

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