Effects of Hydrogen on the Vacancy Formation in Magnesium

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Quenching and annealing experiments with electrical resistivity measurements were applied to magnesium to investigate the formation of thermal vacancies. Two specimens made from materials differing in impurity contents were examined. One of the specimens quenched in a methanol bath at \(-80\) °C from elevated temperatures ranging from \(160\) °C to \(500\) °C revealed a significant decrease in electrical resistance after annealing for 10 min in the bath. Based on the annealing behaviors at low temperatures (\(-100\) °C to \(-60\) °C) after the quenching from \(200\) °C, this decrease is thought to be due to the presence of hydrogen in solution. The other specimen, presumably containing smaller amounts of hydrogen, was quenched in iced water from elevated temperatures (\(200\) °C–\(560\) °C) which yielded results characterized by two thermal activation processes. These processes had the activation energies 54.1 kJ/mol (0.56 eV) and 89.8 kJ/mol (0.93 eV) for the lower and higher quenching temperature ranges, respectively. The former is ascribed to the formation energy of a vacancy interacting with hydrogen and the latter to the intrinsic formation energy of a vacancy. The difference between these energies, 35.7 kJ/mol (0.37 eV), is the binding energy between a vacancy and a hydrogen atom. [doi:10.2320/matertrans.MRA2008082]

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1. Introduction

Compared with aluminum as an example, magnesium has been rarely studied on the self-diffusion and/or the formation and the migration of atomic vacancies that are closely relevant to thermal behavior. It is difficult to refer to many articles on the subject of magnesium, even though the references go back 30–40 years when energetic activity was focused on lattice defects. In spite of these circumstances, there are reports of several techniques regarding the formation energy of vacancies in magnesium: 85.9 kJ/mol (0.89 eV)\textsuperscript{1} and 76.3 kJ/mol (0.79 eV)\textsuperscript{2} by electrical resistivity measurements with quenching from high temperatures, 78.2 kJ/mol (0.81 eV)\textsuperscript{3} by electrical resistivity in thermal equilibrium at high temperatures, 56.0 kJ/mol (0.58 eV)\textsuperscript{4} by dilatometry, and 86.9 kJ/mol (0.90 eV)\textsuperscript{3} by positron annihilation. Tzanetakis et al.\textsuperscript{2} commented on the value of 56.0 kJ/mol (0.58 eV) presented by Janot et al.\textsuperscript{4} because the dilatometric measurement and the lattice constant determination were made on separate specimens which might have had different dislocation distributions. Monti and Savino\textsuperscript{5} pointed out that the formation entropy of a vacancy obtained by Janot et al.\textsuperscript{4} is too small. The other formation energy values are similar in the range 76.3–86.9 kJ/mol (0.79–0.90 eV). The migration energy of a vacancy in magnesium then can be estimated as 49.2–59.8 kJ/mol (0.51–0.62 eV) from the formation energy and the activation energy of the self-diffusion measured by Shewmon\textsuperscript{1} and Combronde and Brebec.\textsuperscript{6} 136.1 kJ/mol (1.41 eV) on average.

Recently, hydrogen storage alloys have received much attention and magnesium is promising base metal of the alloys\textsuperscript{9,10}. It has been reported in the literature that the solid solubility of hydrogen in magnesium is as much as 600 ppm near the melting point in ambient atmosphere\textsuperscript{11} and much hydrogen is contained even in the melt;\textsuperscript{12} this is contrasted with aluminum that dissolves hydrogen at about 1 ppm near the melting point.\textsuperscript{13} More recent studies on hydrogen in metals showed superabundant vacancy formation through dissolution of many hydrogen atoms in the metals under high-pressure hydrogen atmospheres at high temperatures.\textsuperscript{14} It is thought that a vacancy may trap up to six hydrogen atoms in fcc and bcc metals. The binding energy is fairly large, in aluminum at 51.2 kJ/mol (0.53 eV),\textsuperscript{15} for example. These interactions between solute hydrogen atoms and vacancies are also expected to occur in magnesium, although we are aware of no works on this point of view.

The present paper describes a detailed study of the effects of the quenching condition on electrical resistivity of two grades of magnesium. The results are discussed in terms of the interaction of solute hydrogen atoms with vacancies.

2. Experimental Part

Two materials of magnesium used in this study, termed A and B, differ in purity as shown in Table 1. A was made by zone passing ten times in a high-purity (five nines) argon atmosphere from purchased magnesium of 99.95% nominal purity. B is another purchased raw material of 99.97% nominal purity. These are not analyzed for hydrogen content.

The preparation of wire specimens with four leads for electrical resistance measurements is described elsewhere.\textsuperscript{16} Bulk material was hot-forged to a thickness of about 3 mm followed by hot-rolling to a 0.6 mm-thick polycrystalline sheet containing grains of 0.5–1 mm diameter with intermediate annealing at about 400°C in ambient atmosphere.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Material & Purity of original material (%) & Times of zone passing & \(R_{300}/R_{77}\) \\
\hline
A & 99.95 & 10 & 8.521 \\
B & 99.97 & — & 8.439 \\
\hline
\end{tabular}
\caption{Materials and their original purity (except hydrogen), times of zone passing, and ratio of electrical resistance at 27°C to that at \(-196\) °C.}
\end{table}
from which the wire specimen was filed out in the dimensions of $1.2 \times 0.6 \times 150 \text{ mm}^3$ with two leads left at each end, then shaped into a compact sinusoidal form for easy and rapid manipulation on thermal treatments and on resistance measurements together with the four leads supported on a mica sheet. During annealing at 400°C or below in the atmosphere, the dissolution of hydrogen into magnesium due to the decomposition of the magnesium hydroxide surface film can be ignored,\textsuperscript{(17)} as can the sublimation of magnesium.\textsuperscript{(18)} Finally, the surface was chemically polished in dilute nitric acid solution in a specular appearance for the purpose of measurement.

A pure aluminum (99.996%) specimen was also made in the same manner to verify the experimental system.

The heat treatments and quenching methods, presented elsewhere,\textsuperscript{(16)} are as follows. The whole specimen was kept uniformly at quenching temperature for varying time according to the temperature from 20 min at high temperature to 60 min at low temperature: the specimen was set in a narrow, deep space slit on one round face of a cylindrical aluminum block and the temperature of the block was maintained at the quenching temperature in an electric furnace. The reaction of the magnesium specimen with the aluminum block was prevented by using 0.2 mm-thick stainless steel sheets covering the surface of the block in contact with the specimen, the inner surface of the slit and half of the round face. The specimen was subsequently quenched in iced water (0°C) or methanol at −80°C followed by immediate transfer into a liquid nitrogen bath. Throughout the heating, the furnace was filled with high-purity (five nines) argon gas to prevent the specimen from reaction with air. As a result, the aspect of the specimen surface after quenching was kept close to the previous condition.

Electrical resistance was measured in a liquid nitrogen bath by the four-wire method. Variations in the liquid nitrogen temperature due to changes in atmospheric pressure and the mixture of oxygen in ambient air were corrected using a standard specimen of pure aluminum in the bath. The ratio of the temperature coefficient of the resistivity of magnesium to that of aluminum was measured. The value of 0.84 was obtained near the boiling point of liquid nitrogen. Precautions were taken against to minimize the temperature variation in the bath by causing many bubbles at a continuous boil.

3. Results

The resistance increments of pure aluminum on quenching are given in Fig. 1 in relation to the reciprocal of quenching temperature, $T_Q$, (Arrhenius plot), Series 1 or 2 refers to the run seen with decreasing or increasing the temperature. The increments of resistance are shown by $\Delta R / R_A$, where $\Delta R = R_Q - R_A$, $R_Q$ is the as-quenched value of the resistance, and $R_A$ is the resistance after subsequent annealing at 350°C for 1 hour followed by furnace-cooling to room temperature. The annealing at 350°C and the successive furnace-cooling removes excess vacancies, secondary defects and strains on and after the quenching; this annealed-out condition was adopted as a reference of the resistivity of the specimen. Normalization by dividing by $R_A$ can cancel out the effect of change in the size factor\textsuperscript{(19)} of the specimen. For magnesium, the oxidation and sublimation of the surface are particularly worrisome. In Fig. 1 the measured values corresponding to about 200°C and below are distributed around $8.3 \times 10^{-4}$, expressed by $\varepsilon$ in the figure, regardless of the quenching temperature. This is attributed to resistance increments due to internal strain originating from frozen water covering the surface on quenching. A small increment of $\varepsilon$, nonetheless, should be subtracted from the measured values to obtain the contribution of the quenched-in vacancies. This leads to the activation energy of the vacancy formation in aluminum of 63.6 kJ/mol (0.66 eV) that coincides with the measured values reported elsewhere.\textsuperscript{2,5)}

From the given activation energy, the vacancy concentration in aluminum at 300°C is estimated to be about $10^{-6}$. Usually, the amount of hydrogen in aluminum is negligible and can be ignored with respect to vacancy concentration, because the solubility of hydrogen is about 1 ppm near the melting point.\textsuperscript{(13)}

Figures 2 and 3 show an Arrhenius plot of the as-quenched value of resistance increments obtained for magnesium specimens $A$ and $B$, respectively. Quenching was made in an iced water and methanol (−80°C) bath. Resistance measurement after quenching to −80°C was followed by annealing in the same bath for 10 min. The following characteristic behaviors are shown in Figs. 2 and 3.

1. As-quenched values ($\Delta \varepsilon$) are markedly decreased for magnesium $A$ in the range of about 160°C to 500°C as a result
of quenching to \(-80^\circ C\) and subsequent maintenance at the
temperature for 10 min (\(\triangle\)), whereas those of magnesium \(B\)
remain practically unchanged.

(2) The dependences of the as-quenched values for
magnesium \(A\) and \(B\) on quenching temperatures from
100°C to 500°C behave noticeably unlike each other. \(A\)
varies complexly with increasing quenching temperature,
while \(B\) grows monotonically as the temperature is raised.

(3) The resistance increments of as-quenched magnesium
\(B\) are large for 0°C quenching (\(\bigtriangleup\)) compared to
\(-80^\circ C\) quenching (\(\bigtriangledown\)) throughout the range of quenching
temperatures above 200°C, where there are two ranges of temper-
atures that differ in activation energy, i.e. 200°C to 460°C
and above 480°C.

(4) Beyond about 500°C, annealing after quenching has
practically no effect and similar temperature dependence is
exhibited for both \(A\) and \(B\).

To clarify the distinctions between \(A\) and \(B\) noted in (1)
and (2), \(A\) was examined by isothermal annealing at
temperatures (\(T_A\)) of 60°C, –80°C and –100°C after quenching
from 200°C to –80°C. The result is shown in Fig. 4. In the figure the variation of resistance is given by
\(f(t) = [R(t) - R_E]/(R_0 - R_E)\), where \(R(t)\) is the resistance
after annealing for \(t\) seconds at \(T_A\), and \(R_E\) is that after
sufficiently prolonged aging. The activation energy was
obtained by the cross-cut method:20) for \(f(t)\) of 0.8, 0.6, 0.4,
and 0.2, the migration energies of 14.5 (0.15), 16.4 (0.17),
25.1 (0.26), and 32.8 kJ/mol (0.34 eV) are given, respectively
(Fig. 5).

In the next section we discuss the characteristic behaviors
mentioned in (1) to (4) (abbreviated as \(C. B.\) (1), \(C. B.\) (2),
etc., hereafter).

4. Discussion

The formation energy of an atomic vacancy obtained in
the present quenching examination of aluminum is con-
sistent with that found in the literature.2,5) This supports the
validity of the experiment and the data processing adopted
in this study.

4.1 Hydrogen in materials

\(C. B.\) (1) is explainable by considering that point defects,
which migrate with activation energies of 14.5–32.8 kJ/mol
(0.15–0.34 eV) obtained from Figs. 4 and 5, should be
origin of the decrease in resistance shown in material \(A\).
Tzanetakis \textit{et al.}17) conducted electrical resistivity measure-
ments to study the isochronal annealing behavior of highly
purified magnesium containing hydrogen doped by decom-
posing surface hydroxide at high temperatures, and deduced
that the resulting migration energy of 14.5–24.1 kJ/mol (0.15–0.25 eV) is due to the migration of hydrogen. It is thus reasonable to consider that the annealing process in Fig. 4 originates from the migration of hydrogen atoms, because of the equivalency between the activation energy values in Fig. 5 and those obtained by Tzane’takis et al.

Hydrogen content in material B appears to be fairly small compared with material A since the resistance of B after quenching to $-80^\circ\text{C}$ was practically unchanged on successive annealing. Nevertheless, the results of quenching to $0^\circ\text{C}$ (Fig. 3, $\bigcirc$) reveal two regions of quenching temperature higher than about $200^\circ\text{C}$ which differ in activation energy of the thermal process ($C, B, (3)$). The temperature range $200^\circ\text{C}$ to $460^\circ\text{C}$ is similar in that there was complicated behaviour of as-quenched resistance in A, so it is reasonable to expect a proper content of hydrogen in B that affects the thermal process in this range of temperatures.

4.2 Behaviors of vacancies and hydrogen, and variations of resistivity

It is difficult to understand the complicated features of material A exhibited after quenching to $-80^\circ\text{C}$ ($C, B, (2)$) in terms of only the thermally activated process of vacancy formation. The large amount of hydrogen in A leads to the idea that the increases in resistance due to quenching are attributable to the contributions of hydrogen solid-solved again, which has precipitated at lower temperatures, and also to the contribution of created vacancies. This implies that equilibrium hydrogen in the solid solution is frozen-in by the quenching, even though a part precipitates on cooling due to the small migration energy of hydrogen. At near $200^\circ\text{C}$ the increase in resistance of A with the rise in quenching temperature was weakened and thereafter it decreased up to about $250^\circ\text{C}$. This drop in resistance may be due to the formation of vacancy-hydrogen complexes produced by increasing vacancies combined with hydrogen atoms in the solid solution. According to San-Martin and Manchester, $^{11}$ the solid solubility of hydrogen in magnesium is about 60 ppm at $200^\circ\text{C}$, so it is supposed that a comparable or larger amount of hydrogen is contained in A.

The results in Figs. 2 and 3 which show the results of two quenching media, iced water ($0^\circ\text{C}, \bigcirc$) and methanol ($-80^\circ\text{C}, \Delta$), can be explained as follows: owing to the rapid cooling to $0^\circ\text{C}$ of iced water and the relatively high rate of cooling from $0^\circ\text{C}$ to $-80^\circ\text{C}$ of methanol, $^{21}$ many of vacancies and vacancy-hydrogen complexes are quenched-in by iced water quenching, whereas much of the hydrogen in the solid solution is frozen-in by the quenching into methanol ($-80^\circ\text{C}$).

4.3 Vacancies and hydrogen at temperatures above $500^\circ\text{C}$

The following two models are proposed to explain the interactions between the vacancies and hydrogen at temperatures higher than about $500^\circ\text{C}$ ($C, B, (4)$).

(a) At high temperatures near $500^\circ\text{C}$, all of the hydrogen in the solid solution can combine with increased vacancies (fully bound model). If the higher temperature of quenching is selected, no free hydrogen is present, therefore after the quenching the precipitation of hydrogen and the accom-
panying resistance reductions will not take place on subsequent annealing. Regarding vacancy formation at the higher temperature where excess hydrogen available for binding to vacancies is depleted, more vacancies are formed independent of hydrogen. As a result, the vacancies at the higher temperatures may be created by the intrinsic activation energy of formation in magnesium, without reducing the activation energy by binding energy between a vacancy and a hydrogen atom.

(b) At high temperatures near 500°C, it is thought that all of hydrogen in the solid solution can be released from binding with vacancies (free hydrogen model). In this situation, vacancies are formed almost without regard to hydrogen, hence the number of vacancies in equilibrium will be determined by the intrinsic formation energy of the vacancies. If quenching is achieved for the situation that the vacancies and the solved hydrogen are distributed independently throughout the material, the hydrogen in the solid solution will rapidly disappear during cooling through the association with the numerous vacancies and also through precipitations to form voids,\textsuperscript{22)} for example, due to the small migration energy. Consequently, annealing at −80°C after quenching is no longer able to affect electrical resistance.

Both model (a) and model (b) suggest that the formation energy of a vacancy free from hydrogen could be measured by the quenching experiments beyond about 500°C. According to model (a), because of the larger amount of hydrogen in A than in B, the temperature beyond which all hydrogen is bound with vacancies can be expected to be higher for A in accordance with the requirement for more vacancies. However, the experimental results show that this temperature is about 500°C for both the materials, A and B, and thus the temperature does not appear to have been influenced by the hydrogen content. This fact is inconsistent with model (a). Also, if the difference, 49.3 kJ/mol (0.51 eV), between two activation energies, 40.5 kJ/mol (0.42 eV) and 89.8 kJ/mol (0.93 eV), obtained from the results of B is taken as the order of the binding energy of hydrogen to the vacancies (to be discussed in the next section and, as a result, reduced to a smaller value), it is not appropriate to consider hydrogen to be stably bound to the vacancies at temperatures above 500°C; in fact, several examples of other metals exhibiting the same order of binding energy show that hydrogen in metals is released from vacancies at high temperatures.\textsuperscript{23–25)} From the above, it is reasonable to conclude that model (b), stating that hydrogen at high temperatures coexist with the vacancies without interactions, is adequate for magnesium.

4.4 Binding energy between vacancies and hydrogen

Figure 6 represents again the result of 0°C quenching in Fig. 3. In the figure, the activation energy 89.8 kJ/mol (0.93 eV) obtained from experiments at temperatures above 500°C is taken as the formation energy of a vacancy independent of hydrogen. This value nearly coincides with the formation energy reported for vacancies in magnesium.\textsuperscript{1–3,5)} Extrapolation of the straight solid line is denoted by the dashed line. The dotted line, obtained by subtracting the value of the dashed line from the measured points, is taken as the contribution of the vacancies bound with hydrogen, i.e. vacancy-hydrogen complexes, to the electrical resistance. Here, all vacancies could be thought to be bound with hydrogen below 300°C; then the analysis in the temperature range from 220°C to 300°C gives the formation energy of a vacancy bound with hydrogen as 54.1 kJ/mol (0.56 eV). Assuming that hydrogen in the low concentration may be trapped at one atom per vacancy, the binding energy of hydrogen to a vacancy is given as 35.7 (≈ 89.8 - 54.1) kJ/mol (0.37 (≈ 0.93 - 0.56) eV). This value is comparable with the energy of vacancy-hydrogen binding of other metals,\textsuperscript{14)} e.g. 51.2 kJ/mol (0.53 eV) for aluminum.\textsuperscript{15)}

5. Conclusions

Electrical resistivity was measured to investigate magnesium by quenching from high temperatures into iced water (0°C) or methanol at −80°C, and by subsequent annealing at low temperatures (−100°C to −60°C) isothermally after the quenching to −80°C. It is concluded that:

1. Point defects were detected that migrate and annihilate at low temperatures, from −100°C to −60°C under the present experimental conditions. The defects were recognised as hydrogen based on the migration energy of 14.5–32.8 kJ/mol (0.15–0.34 eV).

2. Hydrogen in magnesium is bound with vacancies at relatively low temperatures, whereas it becomes relatively
free with rising temperatures, and, at temperatures near 500°C migrates in the crystal almost without regard to the presence of vacancies.

(3) The formation energy of a vacancy of 89.8 kJ/mol (0.93 eV) was obtained from magnesium, which, because of the low hydrogen content, shows a negligible increase in electrical resistance by hydrogen solution. The estimated formation energy is lowered to 54.1 kJ/mol (0.56 eV) due to binding with hydrogen. These results estimate the binding energy between a vacancy and a hydrogen atom as 35.7 kJ/mol (0.37 eV).

REFERENCES