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HELIUM RELEASE FROM VARIOUS METALS

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HELIUM RELEASE FROM VARIOUS METALS^{*}

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ABSTRACT

The metals aluminum, iron, nickel, and types 304 and 316 stainless steel have been doped with helium by allowing dissolved tritium to undergo radioactive decay. Helium concentrations below 1 atomic part per million were produced. Using high sensitivity, mass spectrometer techniques, helium release has been observed during isochronal and isothermal anneals. At least two release mechanisms are obvious, their respective gas releases occurring at widely separated temperatures.

INTRODUCTION

Recently a considerable amount of work has been devoted to studying the behavior of helium in metals, and in particular to studying the outgassing behavior of helium.¹ Results to date indicate that the helium behavior is more complicated than originally envisioned. The complications appear to be related to the findings that helium atoms, even at concentrations in the parts per million range, combine either to precipitate into bubbles or to form complexes, possibly with point defects.² Because of this aggregation behavior, it has not been possible, as it has for other gases in metals, to determine the diffusivity and the outgassing behavior. To properly examine these properties requires that studies be made at low enough helium concentrations that the competitive process of aggregation does not occur. Further, it is important that the method for introducing helium into the metal lattice be one that results in a homogeneous distribution of helium and also one that does not introduce large concentrations of point defects with which helium atoms can interact. A method ideally fitting the above criteria is that of the radioactive decay of tritium dissolved in the metal to form ^3He . In this study, the tritium decay method is used to examine helium outgassing from various metals at concentrations in the parts per billion range and below.

EXPERIMENTAL PROCEDURE

Samples of aluminum, copper, nickel,³ iron,⁴ and types 304 and 316 stainless steel⁵ were prepared for tritiation. They were rectangular wafers, 13 by 15 mm cut from sheet from 0.125 mm to 1.00 mm thick. Prior to tritiation, the samples were cleaned and vacuum encapsulated to receive a

preliminary anneal at 800°C (600°C for aluminum and 1000°C for stainless steel) for at least 36 ks.

The tritiation and subsequent tritium outgassing procedures were as follows: the metals were placed into a secondarily-contained pressure vessel for tritium exposure.⁶ The vessel was evacuated to about 1 Pa, leak checked, and flushed with deuterium, reevacuated, heated to 300°C, and then filled to 860 kPa with tritium. After isolation from the tritium supply, the vessel's temperature and internal pressure were monitored for 864 ks. During this period of time, the tritium pressure dropped to 710 kPa. The tritium was removed, and then the specimens were outgassed in a different vessel at 250°C and 39 μ Pa for 75.6 ks.

Residual tritium in each specimen was determined by snipping a corner from each, dissolving it in aqua regia, diluting it with distilled water, and using standard liquid scintillation counting techniques.

The concentrations of tritium and helium expected to be introduced into the various metals by the tritiation treatment are shown in Table I. Predicted values for the helium concentrations are based upon the assumptions of equilibrium tritium concentrations⁷⁻¹⁰ during the exposure time and no loss of helium from the samples. The estimated time for diffusion of tritium into the samples at 300°C is roughly 100 s.

Analysis for helium release during isochronal and isothermal anneals was made using a mass spectrometric gas analyzer¹¹ with a sensitivity to measure 10^{10} atoms of helium. This analyzer was periodically calibrated against known helium standards so that the peak height for $m/e = 3$ provided the number of helium atoms released in either a particular temperature interval or in a given annealing time. Blank runs made with

either no sample or untritiated samples showed a uniformly low background. The temperature during the isochronal and isothermal anneals was usually controlled within $\pm 5^{\circ}\text{C}$ using a Pt-Pt+10% Rh thermocouple.

RESULTS AND DISCUSSION

The results for helium outgassing during isochronal anneals of the metals aluminum, iron, nickel, and type 316 stainless steel are shown in Figs. 1 and 2. Release curves are not shown for copper because the helium concentration was below the limit of detectability. The isochronal anneals were made with either 50 or 100 $^{\circ}\text{C}$ temperature intervals and 150, 300, or 600 s time intervals. After the background is subtracted, the peak height plotted on the ordinate is proportional to the amount of helium released at the indicated temperature in the given time interval. The total amount of helium released as obtained from the cumulative peak heights from room temperature to the melting point or 1300 $^{\circ}\text{C}$ is given in Table I. Several interesting comparisons can be made for the ^3He release curves shown in Figs. 1 and 2.

Aluminum

It is surprising that aluminum shows the presence of helium at all, because the tritium solubility at 300 $^{\circ}\text{C}$ is so low⁷ that the predicted helium concentration is below the limit of detectability. It may be hypothesized that as a result of trapping by impurities tritium was present at concentrations above the solubility limit.

In Fig. 1 aluminum shows a maximum release rate near 300 $^{\circ}\text{C}$, roughly at 0.6 the melting point. It is not clear whether this release is the

result of single helium atoms or some form of helium aggregate such as clusters or bubbles. The total release is in the parts per billion range, or an average spacing of roughly 10^3 host atom distances between free helium atoms. If some form of aggregate is present at these low concentrations, then it must be stable with a small number of helium atoms to be able to form at all.

The helium concentration in the two runs shown differed by more than a factor of two and similar behavior was found for the other metals studied. There are two possible reasons for this. First, because of the close stacking of the samples during the tritiation treatment, all samples may not have been charged to the same tritium level. Second, the residual tritium that was not removed by the outgassing treatment (Table 1) produced excess helium during the time before measurement of the helium release. For most cases, the amount of extra helium produced after outgassing but before measurement (typically about 10^{-3} ppm) is not enough to account for the differences. The releases occurred at slightly different temperatures for the two aluminum runs because of differences in specimen size, difficulties in temperature control at low temperatures, and differences in the heating rate.

Iron

The two samples of iron (Fig. 1), with the minor exception of a small peak at 500°C, indicated the same outgassing behavior. The results show a small amount of release at roughly 200°C and a large release near the melting point. As determined by isothermally annealing at 1300°C, the total amount of helium in the samples was much more than was released

during the isochronal anneal to 1300°C. The total amount of helium in the samples could not be determined because the upper limit of the furnace prevented heating specimens through the melting point.

The release at 200°C shown in both of the iron samples is of particular interest. Apparently helium is mobile at temperatures roughly 0.25 the melting point. As shown in Fig. 2, helium is also mobile in nickel in this temperature range. The homologous temperature for this low-temperature release for aluminum is roughly -30°C; thus the aluminum results would not be expected to show the low-temperature outgassing behavior.

A rough calculation of the activation energy for motion of helium in iron at 200°C may be made by assuming a random walk so that the number of atom jumps for diffusion out of the sample in the 600 s time interval is the square of the diffusion distance in the sample half-thickness in units of single jump distances. Using $0.5 a_0$ as the single jump distance and depending on the choice of attempt frequency and geometric factor, an activation energy for motion in the range from 0.4 eV to 0.5 eV is obtained. Such a low activation energy eliminates a substitutional diffusion mechanism thus indicating that the helium is present in interstitial sites. If the 200°C peak is a result of the mobility of single helium atoms, then the prediction of interstitial site occupancy of Bauer and Wilson¹² is confirmed. The activation energy for motion, is in agreement with the prediction for copper (0.45 to 0.71 eV)¹³ but not for nickel (0.08 eV) or for iron (0.17 eV).¹⁴ Furthermore, the outgassing which occurs above 1000°C may then be considered as being due to aggregated helium, presumably bubbles.

Nickel

As previously mentioned, the results for nickel also show helium to be mobile near 200°C, as shown in Fig. 2. These results for the low-temperature helium release in nickel agree reasonably well with results reported by Bauer and Wilson for nickel implanted with 300 keV helium atoms.¹² In addition to the low-temperature release, nickel also shows release at 700°C and above. The first of the two samples measured (run 3) had a much larger release in the range from 700 to 1100°C, possibly because it was tested earlier (Table I) and thus had not lost helium to the free surface. The results for nickel can be interpreted similarly to those for iron. Again, the total helium in the samples could not be determined.

Stainless Steels

The release curves for both types 304 and 316 stainless steel are similar to those for pure iron and nickel. For type 316 stainless steel (Fig. 2), at both high and low temperatures, there is a release that may be considered a result of atomic and aggregated helium, respectively. The low temperature peak occurs at 300°C instead of at 200°C as for iron and nickel. The results for type 304 stainless steel also show a release peak at 300°C. This higher temperature of release suggests trapping of the atomic helium in the stainless steel. As for the iron and nickel, both specimens had the same size and received the same treatment, except for the holding time at room temperature prior to measurement.

Isothermal annealing behavior at high temperature is typical of iron, nickel, and the stainless steels. In Fig. 3 helium release (after background is subtracted) during a given time interval (150 or 300 s) is plotted versus

total annealing time at 1250°C after the isochronal anneal to 1250°C. Two findings should be noted. First, the total helium released in only 1800 s at 1250°C is more than twice that released during the isochronal anneal up to 1250°C. Second, the release rate initially decreases very rapidly but later changes very slowly, maintaining a relatively large release rate at long times. These results are consistent with the previously discussed interpretation that the helium, even at these low concentrations, is present as bubbles at high temperatures. These bubbles would be expected to be present with a distribution of bubble sizes that, in turn, have diffusivities which decrease with increasing size.¹⁵ Thus we can expect that the initial rapid release at high temperature is a result of the rapidly diffusing small bubbles while the continuous release at long times is a result of the larger slow-moving bubbles.

The appreciable helium release at low temperature (~200°C) suggests that helium release was continuously occurring during the 10-day holding time at 300°C, when it was intended to charge the specimens with helium by the tritium decay. Also, helium that was introduced and not released during the tritium exposure could have been released during the tritium degassing at 250°C. Therefore, the helium that was released near 200°C during the isochronal anneals was helium that had been formed subsequent to the tritium outgassing by decay of the residual tritium. The concentration of residual tritium decaying during the time before measurement (Table I) is sufficient to account for the amount of helium observed in the 200°C peak but not sufficient to account for the helium released at high temperature. Thus, during the tritium exposure at 300°C, helium was generated in concentrations sufficiently high to form aggregated helium, possibly

bubbles, which served to trap the helium in the lattice until released at high temperature.

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Table I. Predicted and actual results for generation of helium.

Metal	Run	Time prior to measurement (days)	Equilibrium tritium conc. (ppm) ^a	Residual tritium analyzed (ppm)	Predicted helium conc. (ppm) ^b	Analyzed helium conc. (ppm)
Al	6	15	8×10^{-3}	0.54	1.3×10^{-5}	2.6×10^{-3}
	22	40	8×10^{-3}	0.24	1.3×10^{-5}	6.2×10^{-3}
Cu	4	13	0.14	Unknown	2.3×10^{-4}	None ($< 10^{-5}$)
	11	23	0.14	0.79	2.3×10^{-4}	None ($< 10^{-5}$)
Fe	9	21	8.8	Unknown	1.5×10^{-2}	$> 2.6 \times 10^{-4}$ ^c
	23	53	8.8	Unknown	1.5×10^{-2}	$> 4.6 \times 10^{-4}$ ^c
Ni	3	6	110	1.3	0.18	$> 8.1 \times 10^{-3}$ ^c
	27	54	110	Unknown	0.18	$> 2.9 \times 10^{-3}$ ^c
Type 316 stainless steel	8	20	Unknown	6.1	Unknown	$> 1.6 \times 10^{-3}$ ^c
	12	24	Unknown	2.8	Unknown	$> 2.2 \times 10^{-3}$ ^c

^aBased upon known or extrapolated tritium (or hydrogen) solubility.

^bBased upon equilibrium tritium concentration for full decay time.

^cTotal helium is unknown because sample was not melted.

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FIGURE CAPTIONS

Fig. 1. Isochronal anneals from aluminum and iron. Specified times are times material was held at each temperature.

Fig. 2. Isochromal anneals for nickel and 316 stainless steel. Specified times are times material was held at each temperature.

Fig. 3. Isothermal anneal at 1250°C for nickel.

Hickman - Fig. 1

Hickman - Fig. 2

Hickman - Fig. 3