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Post-irradiation annealing effect on helium diffusivity in austenitic stainless steels

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Abstract

As an experimental basis for helium induced weld cracking of neutron irradiated austenitic stainless steels, helium diffusivity has been evaluated by measuring helium release at high temperature. Isochronal and isothermal experiments were performed at temperatures between 700 and 1300 °C for 304 and 316L stainless steels. In 1 h isochronal experiments, helium was released beginning at ~900 °C and reaching almost 100% at 1300 °C. No apparent differences in helium release were observed between the two stainless steel types. At temperatures between 900 and 1300 °C, the diffusion rate was calculated from the time dependence of the helium release rate to be: $D_0 = 4.91$ cm^2/s, $E = 289$ kJ/mol. The observed activation energy suggests that the release of helium from the steels is associated with the removal of helium from helium bubbles and/or from vacancy diffusion.

1. Introduction

Austenitic stainless steel is the main constituent material used in reactor internal structures both for fission and fusion reactors. For fusion reactors such as ITER, austenitic stainless steels were employed for blanket cooling pipes. The materials contains nickel as a major alloying element and boron as a trace element. Both these elements have a large cross-section for nuclear transmutation by thermal neutrons, which results in significant helium production in addition to helium produced by fast neutrons from (n,α) reactions. The applicable reactions are; ^{10}B(n,α) and ^{58}Ni(n,γ) ^{59}Ni(n,α) ^{56}Fe.

Generation of helium is known to degrade the properties of materials. It has been reported that cracking after welding is caused by helium embrittlement [1,2]. Weld cracks of irradiated stainless steel generally occurred in the weld heat affected zone (HAZ). The cracks were intergranular in nature, and were attributed to nucleation along grain boundaries, coalescence, and growth of helium bubbles from the heating during welding. Therefore, it is important to understand the fundamental behavior of helium diffusion in the high temperature region.

The present work reports a basic study of helium diffusivity in stainless steels by measuring and evaluating the release of helium at high temperature. The activation energy for bulk diffusion of helium has been determined by measuring the helium release for isochronal and isothermal anneals over a series of temperatures in the range of 700–1600 °C.

2. Experimental

2.1. Samples and helium analysis procedure

Four samples of solution heat treated (SHT) 304 and 316L SS were employed in the present work. Sample

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Table 1
Chemical compositions and neutron fluences of irradiated materials[a]

Sample ID	Steel type	Chemical composition (wt%)[b]									Fluence ($\times 10^{25}$ n/m^2, $E > 1$ MeV)
		C	Si	Mn	P	S	Cr	Ni	Mo	Fe	
N-2	304	0.05	0.37	1.75	0.030	0.014	18.14	9.03	–	Bal.	12
N-7	304	0.05	0.51	1.69	0.026	0.006	18.60	9.2	–	Bal.	5
N-8	304	0.05	0.37	1.75	0.030	0.014	18.14	13.6	–	Bal.	1.4
N-10	316L	0.01	0.61	1.47	0.022	0.001	16.40	13.8	2.13	Bal.	7

[a] Irradiation temperature: 288 °C.

[b] Measured before irradiation.

parameters are summarized in Table 1. For the helium release analyses, smaller specimens were cut from each of the original samples. The shape of each specimen was best approximated by a cube or sphere of the same mass.

The helium released from each specimen, as a function of both time and temperature, was determined by isotope-dilution gas mass spectrometry [3] while heating in a resistance-heated tantalum crucible. The absolute amount of ^{4}He released was measured relative to a known quantity of ^{3}He 'spike' added to the furnace at the beginning of each test. Temperature measurements were made using an optical pyrometer calibrated against a dummy crucible in the furnace whose temperature was directly measured using a standard K-type thermocouple to 1200 °C. This calibration was made prior to the start of the measurements, and periodically thereafter. Uncertainty (1σ) in the crucible temperature is estimated to be ±30 °C.

2.2. Helium measurements

Two separate types of helium release measurements were made.

2.2.1. Isochronal measurement

The first type of measurement involved multiple sequential analysis while the temperature of the crucible was maintained at fixed values of 700, 900, and 1100 °C for a 1-h time period, following by a 1-min heating to approximately 1600 °C to melt the specimen. Total cumulative helium release (i.e., the ratio of the helium released to the total helium in the sample) from the sample was measured at the end of each temperature step.

2.2.2. Isothermal measurement

The second type of measurement involved holding the crucible at a constant temperature and measuring the cumulative helium release as a function of time. For these measurements, the crucible temperature was fixed at 900, 1100, 1200, and 1300 °C. For this procedure, helium measurements were made at approximately 5 min intervals within each temperature step.

3. Results and discussion

3.1. Isochronal and isothermal measurements

Type 304 SS (N-2, -7, -10) was employed for these measurements. The results are shown in Fig. 1. Helium release was first observed at ~700 °C and reached ~100% at 1300 °C. At temperatures between 700 and 900 °C, the fractional release was small (0.1–0.5%). The fractional release became significant at ~1100 °C (1 and 13%), and reached ~100% at 1300 °C.

Type 304 and 316 (N-10) was employed for isothermal measurements. The results are shown in Figs. 2–5 as a function of the square root of time divided by the sample radius in accordance with the diffusion model discussed in the next section. The solid lines in each figure are a least-squares linear fit to the overall data set. Although the fractional helium releases show some scatter from specimen to specimen, the data do show roughly linear trends at each of the various temperature steps. The data did not show any observable trends between the 304 and 316L SS.

At 900 °C, the release did not extrapolate to zero at zero time, particularly for Sample N-8. This suggests

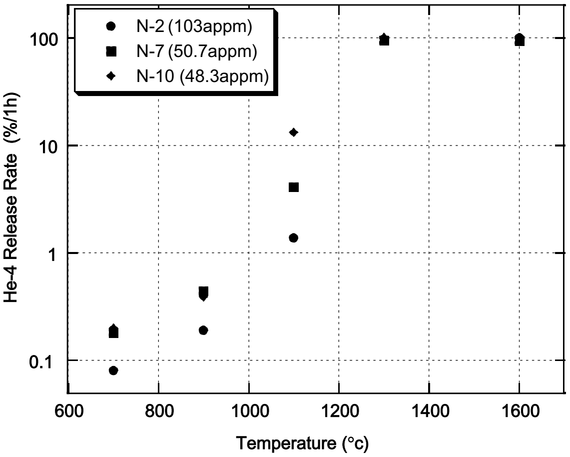

Fig. 1. He-4 release rate for isochronal annealing (1 h).

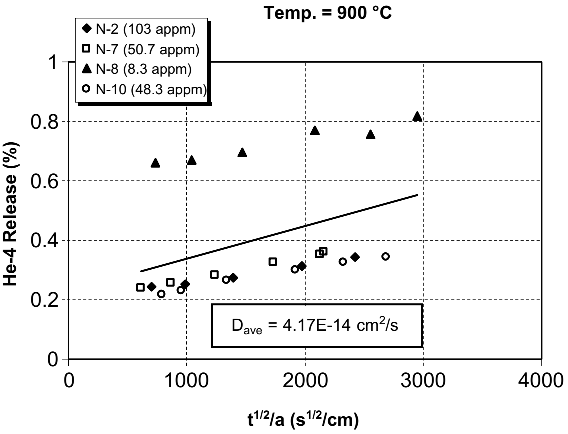

Fig. 2. He-4 release for isothermal annealing at 900 °C.

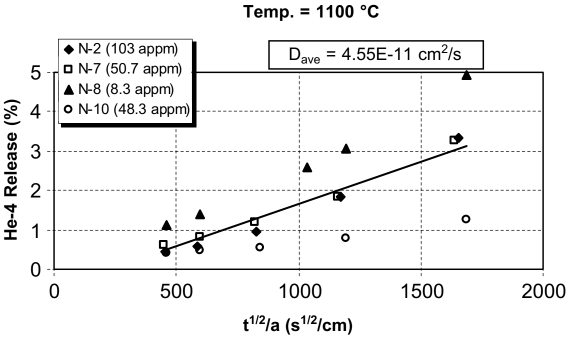

Fig. 3. He-4 release for isothermal annealing at 1100 °C.

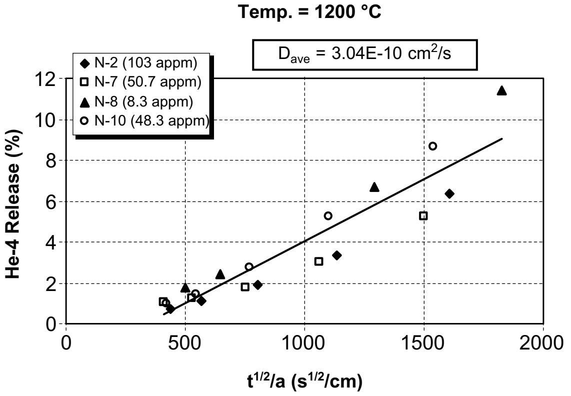

Fig. 4. He-4 release for isothermal annealing at 1200 °C.

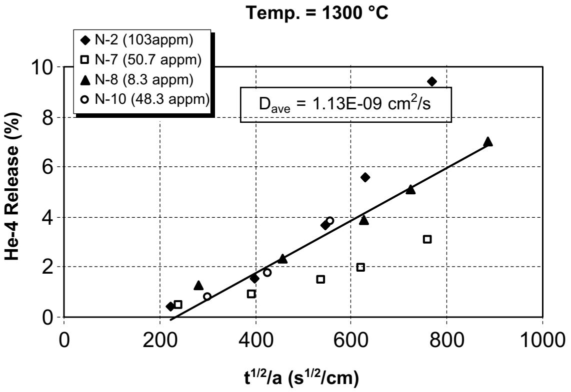

Fig. 5. He-4 release for isothermal annealing at 1300 °C.

that there was an initial helium release from the samples which occurred at a higher rate than after steady-state conditions were achieved. For lower helium concentration, such an initial helium release would result in an offset in the data as seen for Sample N-8. At 1100, 1200, and 1300 °C, the extrapolated helium releases generally fall below zero at zero time, suggesting an opposite trend.

3.2. *Analysis of diffusion rate*

3.2.1. *Diffusion model*

The procedure adopted here was to consider the diffusion system to be an assembly of uniform spherical regions. Assuming the concentration of helium at the surface is always zero, the fraction, f, that has diffused out in time, t, at a given temperature, is given by [4].

$$f = 1 - 6/\pi^2 \Sigma 1/n^2 \exp(-n^2\pi^2 Dt/a^2). \qquad (1)$$

If $\pi^2 Dt/a^2 < 0.01 (f < 0.105)$, Eq. (1) can be approximated by

$$f = 6/a(Dt/\pi)^{1/2}. \qquad (2)$$

Here, a is the equivalent sample radius, n is the order of integration and D is the diffusion constant. Eq. (2) was employed for the analysis of the present experimental data.

3.2.2. *Results of analysis*

In the case where thermal activation processes dominate the diffusion, the diffusion constant obeys the well known relationship

$$D = D_0 \exp(-E/RT), \qquad (3)$$

where E is the activation energy. A plot of $\log D$ vs. $1/T$ is shown in Fig. 6. Here, plots between 1100 and 1300 °C were employed for calculating activation energy because it seems to involve some local effect in 900 °C such as helium trapping at grain boundary. As is indicated in the plot, $\log D$ shows an inverse linear trend. The calculated diffusion parameters are as following; $D_0 = 4.91$ cm^2/s, $E = 289$ kJ/mol $(= 3.0$ eV).

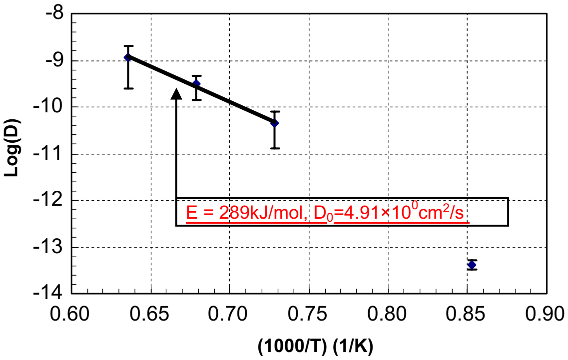

Fig. 6. Arrhenius plot of He-4 diffusion constant.

3.2.3. Diffusion mechanisms for helium release

Helium diffuses via a number of processes before being released. Helium produced by nuclear transmutation is insoluble in stainless steel and thus may exist in interstitial and/or vacancy sites. Interstitial helium is unstable and will very soon encounter a thermal vacancy and then occupy a substitutional site.

Two diffusion mechanisms, i.e., interstitial and vacancy mechanism, are possible for trapped helium atoms [5]. Helium in a lattice site is atomic because of the closed electronic shell of the helium atom from which the metal conduction electrons are shielded out. Therefore, when sufficient thermal energy is given to an atom, it jumps to an interstitial lattice site and then starts to diffuse. Some of the helium will be released as atomic when it is located at the surface of specimen. Other helium will form helium-vacancy complexes and precipitate as bubbles in the matrix or grain boundary.

3.2.4. Activation energy for helium release

Three diffusion processes are important in the helium release; (1) interstitial diffusion, (2) vacancy diffusion, and (3) dissociation of helium atoms in bubbles. The activation energy for each process, and data obtained from the present study are discussed below.

(1) The activation energy for migration of interstitial helium is denoted $E^{\mathrm{m}}\mathrm{He}$. When a helium atom is trapped at a vacancy, the activation energy to jump to an interstitial site is equal to the binding energy ($E^{\mathrm{b}}\mathrm{He}V$) between the helium atom and the vacancy. The activation energy of a helium atom re-trapped in a vacancy is the formation energy of vacancy ($E^{\mathrm{f}}V$). Thus, the activation energy for effective diffusion (E^{eff}) is given by,

$$E^{\mathrm{eff}} = E^{\mathrm{m}}\mathrm{He} + E^{\mathrm{b}}\mathrm{He}V - E^{\mathrm{f}}V. \tag{4}$$

Although experimental values of E^{eff} have not been reported for stainless steel, Hashimoto et al. [6] summarized theoretical values for these parameters values as follows; $E^{\mathrm{m}}\mathrm{He} = 0.2$ eV, $E^{\mathrm{b}}\mathrm{He}V = 2.2$ eV, and $E^{\mathrm{f}}V = 1.9$ eV. From Eq. (4), the activation energy $E^{\mathrm{eff}} = 0.5$ eV (48 kJ/mol). Helium diffusion at high temperatures in fcc structural metals such as nickel [5], gold [7], and aluminum [8] has been studied by ion implantation. For nickel, helium was implanted at temperatures between 800 and 1300 °C and gave an activation energy of $E^{\mathrm{eff}} = 0.81$ eV (78.2 kJ/mol). For gold and aluminum, activation energies of $E^{\mathrm{eff}} = 1.0$ eV (96.5 kJ/mol) and $E^{\mathrm{eff}} = 1.5$ eV (144.7 kJ/mol) were obtained. These values are somewhat higher than calculated from Eq. (4) for stainless steel, indicating that interstitial diffusion in stainless steel should be faster than in other fcc metals.

Activation energy for migration by interstitial mechanisms were considerably smaller than the 3.0 eV (289 kJ/mol) value obtained in this study. Isothermal measurements at 900 °C showed a faster release rate at the initial stage of helium release, suggesting that the helium atoms at the surface of specimen were released before they formed helium-vacancy complexes, possibly as a result of the significantly lower helium concentration in this sample.

(2) The second process is the normal vacancy diffusion mechanism of substitutional impurity atoms. This process is characterized by an activation energy which is usually close to the self-diffusion activation energy. The effective activation energy is given as follows:

$$E^{\mathrm{eff}} = E^{\mathrm{m}}\mathrm{He}V + E^{\mathrm{f}}V, \tag{5}$$

where $E^{\mathrm{m}}\mathrm{He}V$ is the migration energy of atomic helium from lattice sites. A value of E^{eff} for nickel was reported to be 280 kJ/mol (2.9 eV) [7,9]. The values given by Hashimoto [6] are $E^{\mathrm{m}}\mathrm{He}V = 1.2$ eV, $E^{\mathrm{f}}V = 1.9$ eV. This yields a value for E^{eff} of 3.1 eV (299 kJ/mol). This value corresponds the measured activation energy of 3.0 eV (289 kJ/mol); hence, this diffusion mechanism cannot be ruled out.

(3) The diffusion of helium at high temperature is strongly affected by the formation of various helium-vacancy complexes. It appears that in most cases the dissociation energy of helium-vacancy complexes is the rate determining step [9]. The dissociation energy is given by

$$E^{\mathrm{diss}} = E^{\mathrm{m}}\mathrm{He} + E^{\mathrm{b}}\mathrm{He}V. \tag{6}$$

Although values for E^{diss} for stainless steels have not been found, E^{diss} for nickel has been reported to be 231.6 kJ/mol (2.4 eV) [5]. This value also corresponds the measured activation energy of 3.0 eV (289 kJ/mol); hence, the activation energy reported here of $E = 289$ kJ/mol (3.0 eV) appears to correspond with the dissociation energy for helium- vacancy complexes and/or from vacancy diffusion as noted above.

4. Summary

Helium release in austenitic stainless steels have been measured in the high temperature region between 700 and 1300 °C. The following observations from these measurements can be made.

(1) In 1 h isochronal annealing tests, helium release was detectable at temperatures above ~900 °C and reached ~100% at 1300 °C.
(2) The diffusion rate was evaluated using the isothermal data assuming a spherical geometry model.
(3) At temperatures between 900 and 1300 °C, the diffusion parameters could be expressed as: $D_0 = 4.91$ cm^2/s, $E = 289$ kJ/mol. This activation energy suggests that the release of helium from 304 and 316 SS is associated with the removal of helium from helium bubbles and/or from vacancy diffusion.

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