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Dislocation Loop Formation and Growth under *In Situ* Laser and/or Electron Irradiation

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Vacancies and interstitial atoms are primary lattice (point) defects that cause observable microstructural changes, such as the formation of dislocation loops and voids in crystalline solids. These defects' diffusion properties determine the phase stability and environmental resistibility of macroscopic materials under ambient conditions. Although *in situ* methods have been proposed for measuring the diffusion energy of point defects, direct measurement has been limited. In this study, we propose an alternative *in situ* method to measure the activation energy for vacancy migration under laser irradiation using a pulsed laser beam from a laser-equipped high-voltage electron microscope (laser-HVEM). We made *in situ* observations that revealed the formation and growth of vacancy dislocation loops in an austenitic stainless steel during laser irradiation. These loops continued to grow when thermal annealing was performed after laser irradiation at the same temperature. We anticipate that laser-HVEM will provide a new method for investigating lattice defects.

Since the 1960s, interstitial dislocation loops (I-loops) in irradiated face-centred-cubic (fcc) crystals have been conveniently observed *in situ* by high-voltage electron microscopy (HVEM)[1–3]. However, because the clustering of vacancies into dislocation loops may occur rapidly when point defects become supersaturated, due to the methods of high-energy-particle irradiation, plastic deformation, or thermal quenching[4–9], these methods are unsuitable for *in situ* observation.

High-power pulsed laser beams have been used to enhance surface-dependent properties[10–12] because they can deliver controlled energy densities with precise temporal and spatial distributions. Melting and solidification occur within a notably short interaction time, generating a large temperature gradient across the boundary between the melted surface and the substrate, which results in rapid self-quenching and resolidification[13]. Consequently, laser irradiation is expected to introduce supersaturated vacancies into irradiated crystals. HVEM have large specimen chambers, which makes them suitable for *in situ* experimental measures[14]. It is expected that laser-HVEM systems[15] can be used to perform *in situ* observations of vacancy dislocation loop (V-loop) formation and evolution under both laser irradiation and simultaneous laser-electron-beam irradiation.

Because migration plays an important role in vacancy-driven phenomena, the activation energy for vacancy migration (E_{mv}) has attracted considerable interest for many years[16–21]. The E_{mv} of a metal was first measured in the 1950s based on the resistivity change induced by quenching and annealing[9,22]. In the 1970s, E_{mv} was obtained from the temperature dependence of the I-loop growth rate in an *in situ* experiment involving electron-beam irradiation using an HVEM[2]. Investigation of the vacancy equilibration process in pulse-heating experiments by positron annihilation techniques was applied to measure the E_{mv} in the 1980s[23]. Approximately 30 years later, the present study reports the generation of V-loops in SUS316L austenitic stainless steel under laser irradiation and the *in situ* observation of the evolution of these V-loops. Moreover, we propose two new methods for measuring E_{mv}. The chemical composition of the steel is shown in Supplementary Table 1.

Because the formation and evolution of dislocation loops under electron-beam irradiation have been thoroughly studied, this study treats the results of electron-beam irradiation as a standard and compares them with those obtained with laser irradiation.

Results

Faulted loops formed under both electron and laser irradiation. These loops were analysed by the inside-outside technique[24,25], and it was found that Frank I-loops (Burgers vector: $\boldsymbol{b} = 1/3\langle 111 \rangle$ on {111} planes) formed under

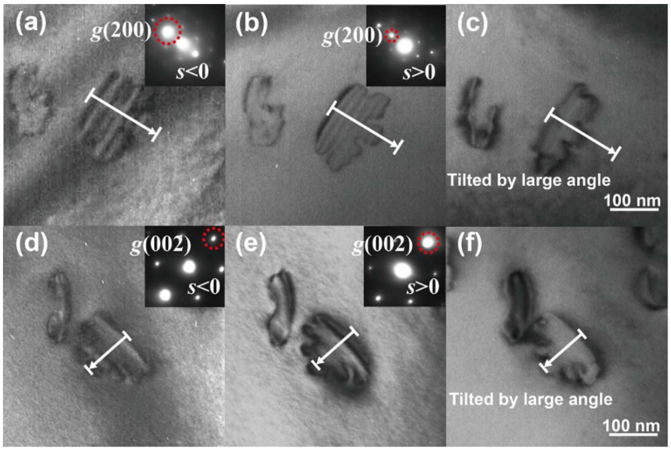

Figure 1 | Analysis of the nature of dislocation loops introduced under different types of irradiation. The white arrows in the figure are used to compare the loop sizes obtained under different conditions. (a)–(c) I-loops formed under electron-beam irradiation. When $\boldsymbol{g}$ (diffraction vector) >0, the loop decreased in size when $\boldsymbol{s}$ (deviation parameter) was changed from $\boldsymbol{s}<0$ to $\boldsymbol{s}>0$, and the sample was tilted at a large angle. (d)–(f) V-loops formed under laser irradiation. When $\boldsymbol{g}>0$, the loop first increased in size when $\boldsymbol{s}$ was changed from $\boldsymbol{s}<0$ to $\boldsymbol{s}>0$. The loop subsequently decreased in size when the sample was tilted at a large angle.

electron-beam irradiation (Figs. 1(a)–(c)) in agreement with previous studies[26,27]. However, Figs. 1(d)–(f) show that a V-loop was formed by laser irradiation; this is the first time that V-loop formation under laser irradiation has been observed *in situ*. Moreover, this loop was also a Frank loop with a Burgers vector of $\boldsymbol{b}=1/3<\bar{1}\;1\;1>$ on {111} planes.

Both loops grew continuously under both types of irradiation, as shown in Figs. 2(a)–(h). After every pulsed-laser irradiation, the specimen was immediately thermally annealed for 90 min at the laser irradiation temperature. The loops introduced by the laser beam also continued to grow during the annealing process (see Figs. 2(i)–(l)).

Fig. 3(a) shows the loop growth rates obtained under different irradiation conditions at 780 K. Based on the loop growth rates at different temperatures, Arrhenius plots for different irradiation conditions were obtained to estimate the E_{mv} (see Fig. 3(b)). In the

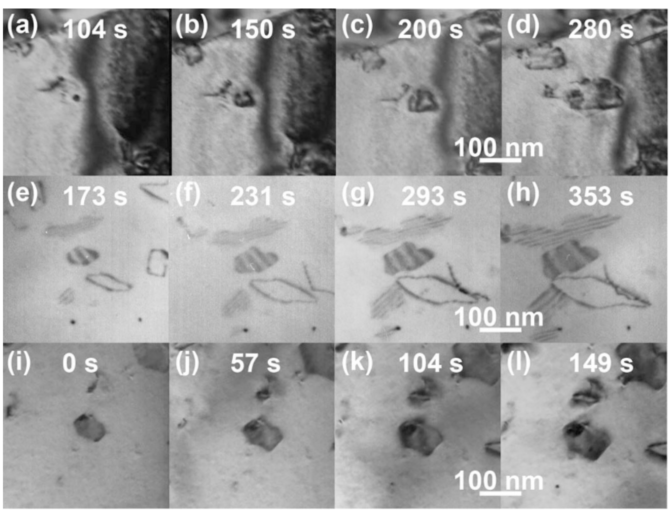

Figure 2 | Dislocation loop growth during different types of irradiation and thermal annealing. (a)–(d) Electron-beam irradiation at 726 K. (e)–(h) Laser irradiation at 806 K (λ = 532 nm). (i)–(l) Thermal annealing at 780 K after laser irradiation (λ = 1064 nm).

present study, the value of E_{mv} for SUS316L steel under electron-beam irradiation was evaluated to be 1.11±0.10 eV, which agrees with previously reported values of 1.04 eV[28] and 1.35 eV[29]. The values of E_{mv} obtained for laser irradiation at wavelengths of 532 and 1064 nm are both 1.13 eV. This value agrees with those obtained by electron-beam irradiation. Figure 3(c) shows the mean loop size plotted against annealing time after pulsed-laser irradiation. Figure 3(d) shows an Arrhenius plot for the thermal annealing. From this plot, the apparent activation energy is estimated to be 1.05±0.14 eV, which corresponds to the E_{mv} value reported in a previous study[28].

Discussion

According to Kiritani *et al.*[2], in the case of Frenkel-pair introduction, the loop growth rate under electron-beam irradiation at temperatures at which vacancies are mobile is given by

$$dR/dt \propto \sqrt{D_v} \propto \exp(-E_{mv}/2kT), \qquad (1)$$

where R is the loop radius, D_v is the vacancy diffusivity, E_{mv} is the activation energy for vacancy migration, k is the Boltzmann constant, and T is the working temperature. Therefore, the Arrhenius slope in Fig. 3(b) is half the value of E_{mv}.

After irradiation by 5-6-ns laser pulses, the heated surface layer (100–150 nm) was rapidly cooled, causing supersaturated vacancies to form. Excess vacancies subsequently diffused into the interior of the specimen and were annihilated at internal sinks, such as dislocation loops. It is thus hypothesised that dislocation loops formed in the interior of the specimen and grew only during the intervals between laser pulses; and the excess vacancy concentration, C_v was constant interior of the specimen because of the excessive pulses. It was assumed that the number of vacancies annihilated at a dislocation loop with a radius of R is proportional to the reaction volume (V) around the loop $V=2\pi R \bullet \pi\left(\sqrt{D_v \Delta t}\right)^2$ (this model is shown in Supplementary Fig. S1 online), where Δt is the interval between laser pulses and $\sqrt{D_v \Delta t}$ is the diffusion length of vacancies during the interval Δt. The increase in the loop radius ΔR is thus proportional to the number of vacancies annihilated at the loop and is inversely proportional to the loop radius: $\Delta R \propto V/R = 2\pi^2 D_v \Delta t$. The average loop growth rate during laser irradiation can then be expressed as

$$dR/dt \approx \Delta R/\Delta t \propto D_v \propto \exp(-E_{mv}/kT) \qquad (2)$$

From equation (2), it can be deduced that the Arrhenius slope of the loop growth rate during laser irradiation is equal to E_{mv}(see Fig. 3(b)). The loops exhibited different growth rates at different temperatures under laser irradiation, which indicates that laser irradiation mainly introduces supersaturated vacancies and does not enhance vacancy migration; rather, vacancy migration is expected to depend on the working temperature.

Excess vacancies were no longer generated during thermal annealing after irradiation by successive laser pulses, and the number of excess vacancies gradually decreased due to annihilation of vacancies at internal sinks, such as grain boundaries or other secondary lattice defects, including dislocation loops in the interior of the material or at the surface sink after long-range diffusion. The excess vacancy concentration, C_v, in the vicinity where a dislocation loop grows can later be expressed as a function of annealing time t as simply ${}^{dC_v}\!/_{dt} = -k_a D_v C_v$ or

$$C_v = C_{v,excess}\exp(-k_a D_v t), \qquad (3)$$

where k_a is the sink strength with the contribution of the other all microstructures within the foil, and $k_a D_v$ is the rate at which vacancies escape from the ambient of the loop because the number of supersaturated vacancies decreases during thermal annealing. $C_{v,excess}$ is the initial concentration of excess vacancies, which cause V-loops to grow in the interior of the specimen prior to annealing. The growth rate of a V-loop during annealing is given by

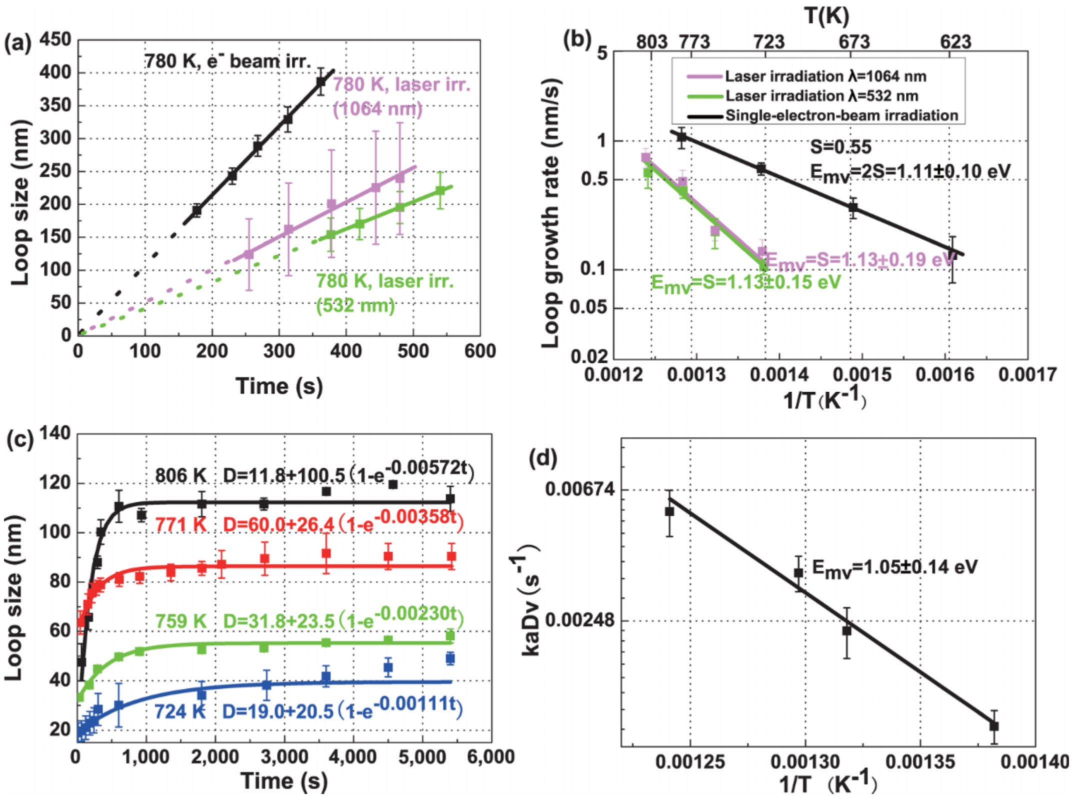

Figure 3 | Loop growth rates and Arrhenius plots under different conditions. (a) Loop size under different irradiation conditions at 780 K. The error bar indicates the maximum and minimum values of the measured loop size. (b) Temperature dependence of the loop growth rate under different irradiation conditions fitted with equations (1) and (2). The error bar represents the standard deviation. (c) Mean loop size vs. annealing time after laser irradiation ($\lambda = 1064$ nm) fitted with equation (5). D denotes the diameter (loop size) of the loop ($D = 2R$). The error bar indicates the maximum and minimum values of the measured loop size. (d) Arrhenius plot of the exponential factor in equation (5). The error bar indicates the standard deviation.

$$dR/dt = \frac{1}{b} D_v C_v = \frac{C_{v,excess}}{b} D_v \exp(-k_a D_v t), \qquad (4)$$

where b is the magnitude of the Burgers vector $\boldsymbol{b}$. Thus, the change in loop size due to thermal annealing can be expressed as

$$R(t) = R_0 + \frac{C_{v,excess}}{bk_a}[1 - \exp(-k_a D_v t)], \qquad (5)$$

where R_0 is the loop radius at $t = 0$ (i.e., the measurement start time), and $k_a D_v$ is proportional to $\exp(-E_{mv}/kT)$. The mean loop size plotted against annealing time is shown in Fig. 3(c). An Arrhenius plot of the exponential factor in equation (5) is shown in Fig. 3(d). The apparent activation energy corresponds to the value of E_{mv} obtained from equations (5) and (2).

Only laser- and single-electron-beam irradiation was performed in the present study. Such irradiation is expected to introduce and control V- and I-loops in metals, depending on which of the two quantum beams is employed. Laser-HVEM can also perform simultaneous irradiation by laser and electron beams, but the details of the formation and evolution of loops (defects) under dual-beam irradiation depend on the laser- and electron-beam intensities; we are currently investigating this and will discuss the results elsewhere. Supplementary Fig. S2 shows models of loop formation under electron-beam irradiation, laser irradiation, and simultaneous electron-beam and laser irradiation.

In summary, *in situ* observations of the formation and evolution of vacancy dislocation loops in an fcc crystal were realised for the first time under laser irradiation by laser-HVEM. Laser irradiation mainly introduces supersaturated vacancies. It is expected that V- or I-loops can be introduced and controlled by irradiation with laser and electron beams, respectively. Two new methods were proposed to determine the activation energy for vacancy migration; the values of E_{mv} obtained through electron irradiation, laser irradiation, and thermal annealing are in good agreement with previously reported values. Based on the experimental results, the average value of E_{mv} under different conditions of electron-beam irradiation, laser irradiation, and thermal annealing for SUS316L stainless steel was determined to be 1.10 ± 0.15 eV. Laser-HVEM is thus expected to provide a new method for investigating lattice defects.

Methods

In this study, solution-treated SUS316L austenite stainless steel was investigated. Sheets were prepared by mechanical thinning to a thickness of less than 0.15 mm. Disks measuring 3 mm in diameter were punched from the sheets and electropolished

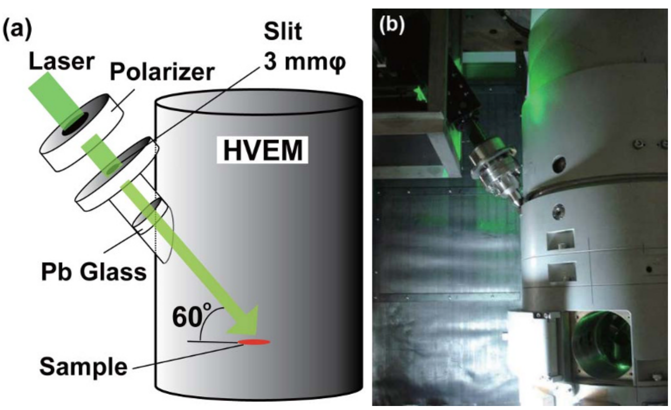

Figure 4 | Laser-HVEM system used in this study. (a) Schematic of laser-HVEM system. (b) Photograph of laser-HVEM system.

for irradiation experiments. In this experiment, the irradiated area had a foil thickness of 450–600 nm.

A Nd:YAG laser was installed outside of the chamber of an H-1300 high-voltage electron microscope above the specimen holder. A linearly polarised laser beam passed through a quartz window and irradiated the specimen at an angle of 60°, as shown in Fig. 4(a); a photograph of the equipment is shown in Fig. 4(b). Because no optical focusing lens was employed in this study, the laser-beam intensity was assumed to be equal over the entire observation region of the specimen.

Laser irradiation by 1200 pulses (10 min) was performed at 723–803 K, a temperature at which vacancies in the metal are highly mobile. The repetition rate of the laser pulses was 2 Hz, and the pulse duration was 5-6-ns. The average energy densities of the laser beam were measured to be 24 and 104 mJ/cm^2 at wavelengths of 532 and 1064 nm, respectively. Because these energy densities are much lower than those at which the surface modification occurs (1–30 J/cm^2)[13], the effects of laser irradiation on the specimen surface were considered to be negligible. During laser irradiation, the electron-beam intensity was kept as low as possible to minimise the effects of electron-beam irradiation on the specimen.

Electron-beam irradiation was performed at 623, 673, 723, and 773 K using a high-voltage electron microscope at 1000 kV with a damage rate of 2×10^{-3} dpa/s. All specimens were observed *in situ* along the (110) plane.

The inside-outside technique was carried out by a JEM-2000ES transmission electron microscope (TEM).

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Author contributions

Z.B.Y. performed the experiment, collected and analysed data, and wrote the paper; N.S. analysed data and derived the new equations; S.W. designed the study, analysed data, and assisted with writing the paper; and M.K. was involved in the study design. All authors discussed the results.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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