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Point defect behavior in electron irradiated V–4Cr–4Ti alloy

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Abstract

To investigate the migration behavior of interstitials and vacancies in vanadium alloy V–4Cr–4Ti, high purity V alloys were irradiated with 2 MeV electrons using a high voltage electron microscope (HVEM) and 28 MeV electrons using a electron linear accelerator. Interstitial type dislocation loops formed quickly in all cases of HVEM irradiation. The saturation density of the dislocation loops was independent of irradiation temperature and defect production rate at temperatures in the range of 323–448 K. However, the logarithm of saturated dislocation loop density was inversely proportional to the irradiation temperature, and dislocation loop density was directly proportional to the square root of the defect production rate above 448 K. The dissociation energy of the interstitial-impurity complex in V–4Cr–4Ti alloy was estimated to be 1.1 eV from the HVEM experiment. It was found from positron lifetime measurements that the vacancies form vacancy clusters at 373 K.

1. Introduction

A vanadium alloy V–4Cr–4Ti has been proposed for its use as a structural material in a fusion reactor because of its low activation properties, good strength at elevated temperatures and favorable mechanical properties. Numerous experiments have been carried out to investigate the microstructural evolution and changes in mechanical properties due to irradiation. Fundamental studies on the V–4Cr–4Ti alloy, such as the behavior of point defects and defect clusters, however, are only a few. Thus, little progress has been made in understanding the mechanism of microstructural change, and estimating the evolution of the microstructure by computer simulation based on an experimental database. On the other hand, it is well known that interstitial impurities such as O, N and C result in a loss of ductility and toughness of V alloy [1–4], therefore, the removal of interstitial impurities O, N and C is important in the fabrication of large, high-quality ingots of V–4Cr–4Ti alloy. Recently, a high-quality V–4Cr–4Ti alloy was developed by the National Institute for Fusion Science (NIFS) [5], in which there is much less O impurity than that produced by the US DOE program. In the present study, the migration behavior of interstitials and vacancies in high-quality V–4Cr–4Ti alloy irradiated by electrons were investigated, and the migration energy of interstitials and temperature of vacancy cluster formation by vacancy migration were obtained.

2. Experimental procedure

Two kinds of high-quality V–4Cr–4Ti alloys developed by NIFS, named NIFS-HEAT-1 and NIFS-HEAT-2, were used in the present study. NIFS-HEAT-1 alloy contained 181 wt ppm O, 88 wt ppm N and 67 wt ppm C, whereas NIFS-HEAT-2 alloy, in which O impurity was decreased and N, C impurities was at the same level, contained 158 wt ppm O, 84 wt ppm N and 62 wt ppm C. In order to investigate the migration energy of interstitials in V alloy, well annealed samples were irradiated with 2 MeV electrons using high voltage electron microscope (HVEM) at Osaka University. The irradiation direction was along the ⟨1 1 1⟩ direction of samples. In situ observations of microstructural evolu-

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tion under imaging conditions of g[1 1 0] were carried out at temperatures in the range of 289–623 K with an electron beam intensity of 1.8×10^{23} to 3.7×10^{24} e/m^2 s, which corresponds to a dpa rate of 1.4×10^{-3}–3.0×10^{-2} dpa/s (displacement per atom/s). In order to investigate the migration behavior of vacancies, bulk samples were irradiated with 28 MeV electrons using a electron linear accelerator in Kyoto University at 100 K. The irradiation dose was 4.0×10^{22} e/m^2, which corresponded to 2.4×10^{-4} dpa. After irradiation the samples were stored at 77 K. Isochronal annealing was carried out at temperatures in the range of room temperature (RT) to 673 K, and the temperature was maintained for 30 min at each temperature above RT. The recovery of vacancies was examined by positron lifetime measurements and the coincidence Doppler broadening (CDB) method at RT.

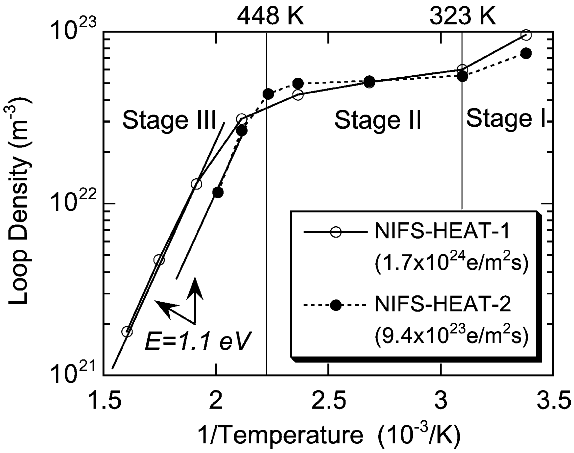

Fig. 2. Arrhenius plot of saturation loop density in NIFS-HEAT-1 and NIFS-HEAT-2.

3. Results

3.1. Microstructural evolution induced by HVEM

Fig. 1 shows the typical microstructural evolution in NIFS-HEAT-1 irradiated by HVEM at several temperatures. Interstitial type dislocation loops were observed at all temperatures. The Arrhenius plot of saturation loop density in NIFS-HEAT-1 and NIFS-HEAT-2 is shown in Fig. 2, where the irradiation intensity in NIFS-HEAT-1 is higher than that in NIFS-HEAT-2. In both V alloys, the temperature dependence of loop density can be divided into three temperature regimes. In stage I where the temperature was lower than 323 K, dislocation loops were formed with high density and the loop density in NIFS-HEAT-1 was slightly higher than that in NIFS-HEAT-2. In stage II where the temperature was from 323 to 448 K, the change of loop density was small, and the loop density was almost the same in both V alloys. In stage III where the temperature was higher than 448 K, loop density decreased rapidly, and the logarithm of loop density was proportional to the reciprocal of temperature. Similar to that in stage I, the loop density in NIFS-HEAT-1 also in stage III was higher than that in NIFS-HEAT-2.

Fig. 3 shows the formation of dislocation loops at 373 and 523 K in NIFS-HEAT-1, which belonged to

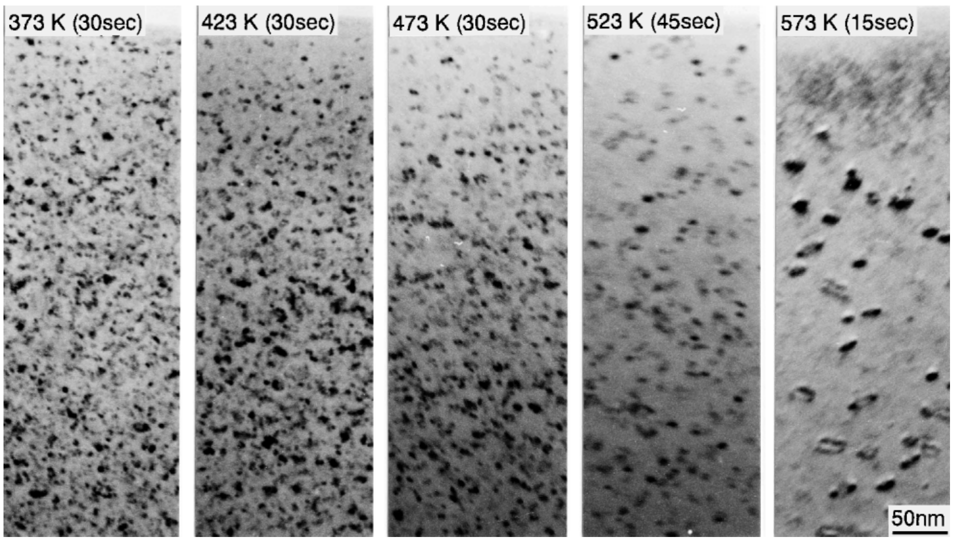

Fig. 1. Typical microstructural evolution in NIFS-HEAT-1 irradiated by HVEM with a beam density of 1.7×10^{24} e/m^2 s at several temperatures. The irradiation direction was along with ⟨1 1 1⟩ direction, and observations were made under imaging conditions of g[1 1 0].

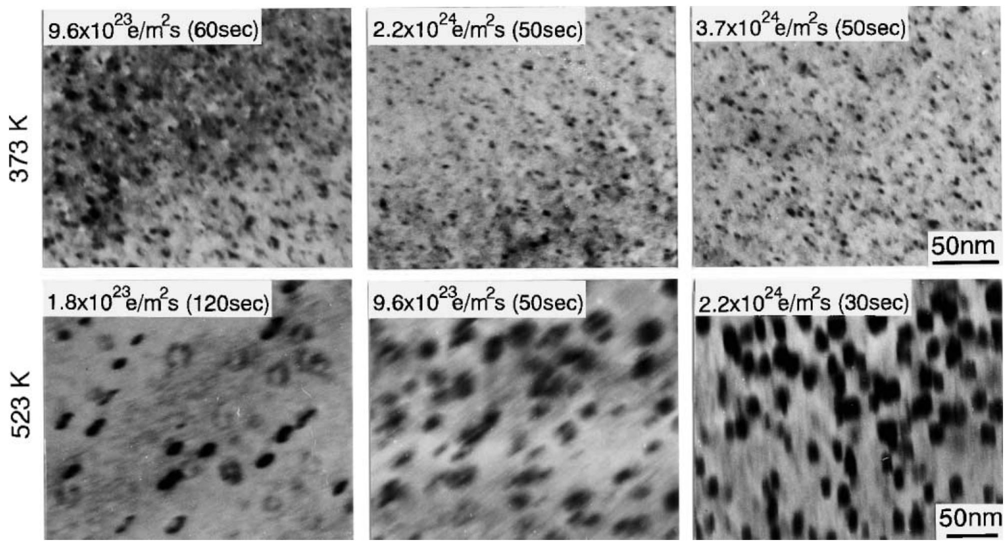

Fig. 3. Typical microstructural evolution in NIFS-HEAT-1 at 373 and 523 K with different irradiation intensities.

stages II and III, respectively, under different irradiation intensities. The irradiation intensity dependence of dislocation loop density is plotted in Fig. 4. In stage II, the loop density was almost independent of irradiation intensity. In stage III, on the other hand, the loop density was proportional to the square root of irradiation intensity.

3.2. Isochronal recovery of vacancies induced by electron irradiation at low temperature

Vacancy recovery in NIFS-HEAT-1 examined by positron lifetime measurements is shown in Fig. 5, where the irradiation temperature was 100 K, while the isochronal annealing was started from RT. τ_m is the positron mean lifetime. The shorter lifetime τ_1 mainly comes

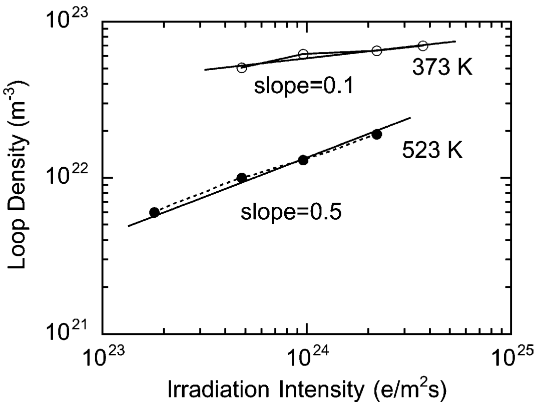

Fig. 4. Beam flux dependence of loop density in NIFS-HEAT-1 in stages II and III.

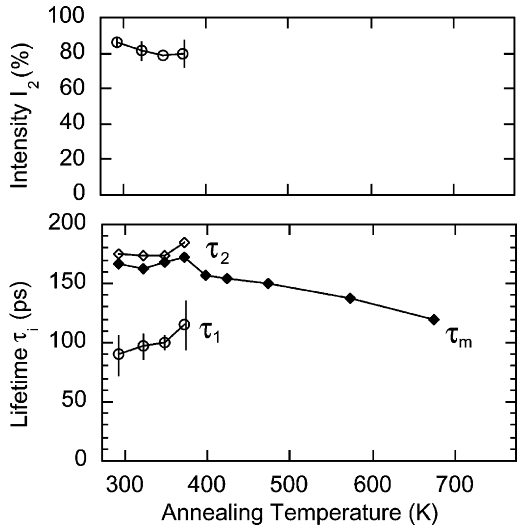

Fig. 5. Changes of positron lifetime and intensity in NIFS-HEAT-1 during the isochronal annealing experiment after irradiation with 28 MeV electrons at 100 K.

from free positrons in the matrix, and the longer lifetime τ_2 results from positrons trapped at defects, such as microvoids. After irradiation, the longer lifetime τ_2 was (175 ± 3.8) ps, and its density was 85.9%. The longer lifetime τ_2 did not change during annealing from RT to 348 K. The longer lifetime τ_2 increased to (185.1 ± 4.2) ps when the temperature increased to 373 K. Two-lifetime-component analysis of measured lifetime spectra could not be carried out when the temperature was higher than 398 K. The mean lifetime τ_m decreased with increasing annealing temperature, and decreased near to

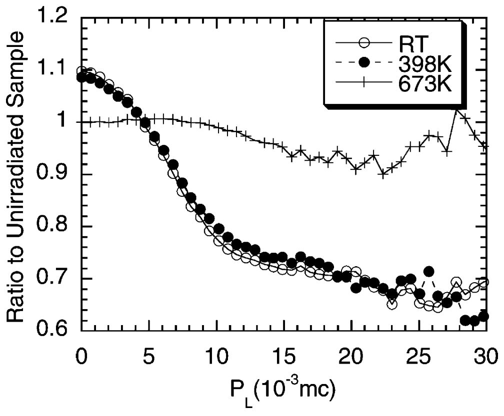

Fig. 6. Typical change of normalized CDB spectra after irradiation with 28 MeV electrons at 100 K. The curves are ratios of CDB spectra in the irradiated sample to those in the well annealed reference sample.

the lifetime 115 ± 0.6 ps of unirradiated V alloy after annealing at 673 K.

The CDB spectrum is strongly influenced by changes in size and density of vacancy agglomerates, and the formation of precipitates [6]. CDB measurements were made after annealing in the present study. They were used to investigate the total vacancy content changes at temperatures higher than 398 K, where the vacancy information could not be obtained from positron lifetime measurements. Fig. 6 shows typical change of normalized CDB spectra, which is the ratio of CDB spectra in the irradiated sample to that in well annealed reference sample, during isochronal annealing. If the ratio is close to 1, the difference in microstructure between irradiated and reference samples is small. P_L is the momentum of the core electron. Same as the results for positron lifetime, the ratio curve of CDB spectra did not change from RT to 348 K. It changed for annealing temperatures larger than 398 K, and approached that of the reference sample at 673 K. In addition, the formation of precipitates was not confirmed by CDB spectra during the annealing.

4. Discussion

4.1. Migration energy of interstitials in V alloy

The analysis method for HVEM was developed by Yoshida and Kiritani based on the chemical rate theory, where di-interstitials were stable dislocation loop nuclei [7]. According to Yoshida and Kiritani, the temperature dependence of an interstitial type dislocation loop density in impurity-containing metals can be divided into four stages. At a very low temperature or stage I, where the mobility of an interstitial is extremely low and interstitials do not reach impurities to form loop nuclei, the saturated loop density C_L is proportional to $P^{1/2}M_I^{-1/2}$, where P is production rate of point defects and increases with increasing electron beam intensity. M_I is interstitial mobility, and can be expressed by $v_0 \exp(-E_m^I/kT)$; E_m^I is the migration energy of the interstitial, and v_0, k, and T are the frequency factor, Boltzmann constant and temperature, respectively. At low temperature or stage II, where interstitials are absorbed by impurities to form loop nuclei, the saturation loop density C_L is determined by the concentration of impurities. C_L is independent of defect production rate P. At medium temperature or stage III, where the interstitial-impurity complex is not stable and dissociates during irradiation, the loop density C_L is given by $C_L \propto (P/M_b)^{1/2}$, therefore, the loop density is proportional to $P^{1/2}$. The dissociation rate of the interstitial-impurity complex M_b is defined as $v_0 \exp(-(E_m^I + E_b)/kT)$. E_b is the binding energy of the complex. At high temperature or stage IV, where the dissociation probability of an interstitial-impurity complex is higher than the formation probability of di-interstitials, the loop density becomes very small.

The three stages observed in the present HVEM experiments in both NIFS-HEAT-1 and NIFS-HEAT-2 corresponded to stages I, II and III of the rate theory analysis mentioned above. In stage I where the temperature was lower than 323 K, the temperature dependence of loop density was difficult to extract accurately since the experimental data were not sufficient and the loop density was too high to be measured exactly. In stage II where the temperature range was from 323 to 448 K, the loop density was almost independent of temperature. In stage III where the temperature was higher than 448 K, the logarithm of the loop density was proportional to the reciprocal of temperature. Following the rate theory analysis, the dissociation energy of the interstitial-impurity complex, i.e., the sum of the migration energy of an interstitial and binding energy between an interstitial and an impurity, is concluded to be 1.1 eV as shown in Fig. 1. Hayashi et al. also investigated the migration behavior of interstitials in V–4Cr–4Ti alloy [8]. They obtained a dissociation energy for the interstitial-impurity complex of 1.0 eV, which agrees with our results.

Furthermore, the loop density is independent of the defect production rate in stage II and proportional to the square root of the defect production rate in stage III as shown in Fig. 4. It is suggested that loops in V alloys are nucleated at Ti-trapping impurities in V alloys, such as O, N and C, since Ti in V is a very strong trap for interstitials O, N and C [9,10]. Although the concentration of the main impurity O was different in NIFS-HEAT-1 and NIFS-HEAT-2, the saturation loop density in stage II was the same. It seems that Ti–O complex is not the main nucleus of loops. On the other hand, stage II of the temperature dependence of loop density is not present in pure V [11], which also contains O, N and C impurities. This also supports the important role of the Ti in V–4Cr–4Ti alloy in loop formation.

4.2. Vacancy migration in V alloy

After the annealing at RT, the longer lifetime τ_2 was 175 ps, which is thought to be a single vacancy lifetime in V–4Cr–4Ti alloy because the calculated vacancy lifetime was 181 ps in pure V [12]. The longer lifetime τ_2 was almost constant at temperatures lower than 348 K, and increased to 185 ps at 373 K. This means that vacancies were mobile at 373 K and thus could form di- or tri-vacancies. The longer lifetime τ_2 could not be obtained when the temperature was higher than 398 K. This implies that the tiny vacancy clusters dissociated and the density of vacancy clusters decreased too low to be measured by positron lifetime measurement. The HVEM results indicate that the binding energy between the interstitial and impurity is lower than 1.1 eV. It is possible for the interstitial-impurity complex to dissociate during 30 min of annealing at temperatures higher than 398 K. The vacancies are annihilated by absorbing interstitials.

5. Conclusion

The migration behavior of interstitials and vacancies in V–4Cr–4Ti alloys has been studied. It was found that the nucleation of interstitial type dislocation loops is affected strongly by the impurities such as O, N, and C. The interstitial-impurity complex is assumed to be the nucleus of the dislocation loop. The dissociation energy for the interstitial and impurity pair is 1.1 eV. It is also concluded that the vacancies become mobile at 373 K. The tiny vacancy clusters absorb the interstitals dissociated from the interstitial-impurity complex at higher temperatures and disappear.

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