Defect Formation Processes in Fe-Cr-Ni Alloys by Neutron Irradiation under Thermal Cycles

Q. Xu*, N. Yoshida** and T. Yoshiie*

*Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka-fu 590-04, Japan

**Research Institute for Applied Mechanics, Kyushu University, Kasuga, Fukuoka 816, Japan

It had been reported that the effects of cyclic temperature change on the radiation induced microstructural evolution in Fe-Cr-Ni alloys were very strong and complicated. In order to understand these results, accumulations of defects under varying temperature irradiations were numerically calculated based on the rate theory for defect clustering. The results indicate the microstructural evolution under varying temperature irradiation as follows. Vacancy-predominant condition appears after changing the temperature from low to high due to the decomposition of small vacancy clusters, which had formed during the low temperature irradiation, by reacting with interstitials produced by the irradiation at the high temperature. Interstitial clusters, therefore, shrink, while vacancy clusters grow by absorbing the excess vacancies. In the case of temperature change from high to low, on the other hand, the interstitial-predominant condition is held throughout the whole irradiation period, and hence interstitial clusters grow, while vacancy clusters shrink. In the cyclic temperature irradiation, the large interstitial and vacancy clusters are difficult to be formed because these clusters grew and shrank repeatedly during the temperatures changed periodically.

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I. Introduction

Properties of materials, such as strength and thermal and electric conductivities, are sensitive to the microstructure. It is known that the evolution of damage microstructure depends on the total dose, dose rate, primary knock-on atoms (PKA) spectrum and the irradiation temperature. Recently, it was demonstrated that temperature variation during irradiation influences the damage microstructures remarkably. For example, some fission neutron irradiation studies showed that small additional irradiation below the designed temperature, which occurs often during the start-up and shutdown processes of the reactor, changed microstructures completely from those developed by the totally isothermal irradiation⁽¹⁾⁻⁽⁴⁾. Since more frequent temperature variation is expected in fusion reactors⁽⁵⁾, it is necessary to understand the influence of temperature variation on microstructural evolution in fusion environment. Cyclic temperature neutron irradiations of 473/673 and 573/723 K, therefore, were proposed and carried out recently at the Japan Materials Testing Reactor (JMTR)⁽⁶⁾.

The details of microstructural evolution in Fe-Cr-Ni model austenitic alloys by cyclic temperature irradiations were reported by the present authors⁽⁷⁾. Some results are shown in Fig. 1, which is the comparison of microstructures formed by constant temperature irradiations at 473, 573, 623 and 673 K and those formed by cyclic temperature irradiations at 473/673 and 573/723 K. It shows that the effects of cyclic temperature on microstructural evolution are strong and complicated. Namely, against the simple expectation that microstructure of 473/673 K-

irradiation would be intermediate of those at 473 and 673 K, interstitial loop density of the cyclic temperature irradiation was much lower than that of the 673 K-irradiation. This result indicates not only that nucleation of the loops at 673 K was suppressed but also that most of the interstitial loops formed at 473 K disappeared in the subsequent irradiation at 673 K. In the case of an Fe-16Cr-17Ni-0.25Ti alloy, on the other hand, unexpectedly dense small voids were observed. In the present work, therefore, numerical calculations of defect clustering processes based on the rate theory were carried out to understand these "unexpected" phenomena under cyclic temperature irradiation.

II. Outline of the Modeling

Since the migration of point defects, such as interstitials and vacancies formed by irradiation, plays a substantial role in microstructural evolution in metals, it is important to inspect the behavior of these mobile defects under varying temperature irradiation. In the present work, their behavior was described by the rate theory⁽⁸⁾⁽⁹⁾ assuming the following single clustering model:

- (1) only interstitials and vacancies are assumed to be mobile,
- (2) thermal dissociation of defect clusters is neglected,
- (3) effects of cascade collisions, such as inhomogeneous defect production and spontaneous cluster formation, are not included.

Throughout this paper, the concentrations are fractional units, i.e. $C(n)$ represents the concentration of clusters containing n defects per lattice site in the matrix.

Fig. 1 Typical microstructures formed in Fe–Cr–Ni at various temperature conditions denoted in the pictures.

The concentrations of interstitial clusters $C_i(n)$ and vacancy clusters $C_v(n)$ can be expressed as

$$\begin{aligned} \frac{dC_i(1)}{dt} = & P - (\alpha_1^I + 2\beta_1^I)C_i(1) - \sum_{n=2}^N \beta_n^I C_i(n) \\ & - \sum_{n=1}^N \beta_n^V C_v(n) - \beta C_s + \alpha_2^I C_i(2) \end{aligned} \quad (1)$$

$$\frac{dC_i(2)}{dt} = \beta_1^I C_i(1) - (\beta_2^I + \alpha_2^I)C_i(2) + \alpha_3^I C_i(3) \quad (2)$$

⋮

$$\begin{aligned} \frac{dC_i(N)}{dt} = & \beta_{N-1}^I C_i(N-1) - (\beta_N^I + \alpha_N^I)C_i(N) \\ & + \alpha_{N+1}^I C_i(N+1) \end{aligned} \quad (3)$$

and

$$\begin{aligned} \frac{dC_v(1)}{dt} = & P - (\beta_1^V + 2\alpha_1^V)C_v(1) - \sum_{n=2}^N \alpha_n^V C_v(n) \\ & - \sum_{n=1}^N \alpha_n^I C_i(n) - \alpha C_s + \beta_2^V C_v(2) \end{aligned} \quad (4)$$

$$\frac{dC_v(2)}{dt} = \alpha_1^V C_v(1) - (\beta_2^V + \alpha_2^V)C_v(2) + \beta_3^V C_v(3) \quad (5)$$

⋮

$$\begin{aligned} \frac{dC_v(N)}{dt} = & \alpha_{N-1}^V C_v(N-1) - (\beta_N^V + \alpha_N^V)C_v(N) \\ & + \beta_{N+1}^V C_v(N+1). \end{aligned} \quad (6)$$

The rate constants β_n^I (or α_n^I) describe the absorption of an interstitial (or a vacancy) at interstitial clusters of size n . While the rate constants β_n^V (or α_n^V) describe that of an interstitial (or a vacancy) at vacancy clusters of size n . P is Frenkel pair production rate per atom and C_s is

the efficiency of permanent sinks. The rate constants β_n^I and β_n^V can be written as

$$\beta_n^I = Z_{II}(n)C_i(1)M_I \quad (7)$$

and

$$\beta_n^V = Z_{VI}(n)C_i(1)M_I, \quad (8)$$

where $Z_{II}(n)$ and $Z_{VI}(n)$ are the number of spontaneous reaction sites with an interstitial around an interstitial cluster and a vacancy cluster of size n , respectively. M_I is the jump rate (or mobility) of an interstitial. The rate constants α_n^I and α_n^V can be written as

$$\alpha_n^I = Z_{IV}(n)C_v(1)M_V \quad (9)$$

and

$$\alpha_n^V = Z_{VV}(n)C_v(1)M_V, \quad (10)$$

where $Z_{IV}(n)$ and $Z_{VV}(n)$ are the number of spontaneous reaction sites with a vacancy around a interstitial cluster and a vacancy cluster of size n , respectively. M_V is the jump rate of a vacancy. In the present calculation, $Z_{ij}(n)$ are assumed to be proportional to the square root of the cluster size n , where the subscripts i and j denote either interstitials or vacancies.

The jump rates of an interstitial and vacancy are given by

$$M_I = \nu \exp(-E_m^I/\kappa T) \quad (11)$$

and

$$M_V = \nu \exp(-E_m^V/\kappa T), \quad (12)$$

respectively, where ν is an attempt frequency; κ is Boltzmann's constant; T is the absolute temperature; and E_m^I and E_m^V are the migration activation energy of an

interstitial and a vacancy, respectively.

III. Analysis of Defect Clustering under the Cyclic Temperature Irradiation

In order to analyze the accumulation of defects under the cyclic temperature irradiation, numerical calculation was carried out by using the rate equations described in the previous section. To save the calculation time, defect processes were calculated only during the first stage of increase temperature (i.e. changing temperature from 473 to 673 K) and the first stage of decrease temperature (i.e. changing temperature from 673 to 473 K), though irradiations at 473 and 673 K were repeated six times in the neutron irradiation experiment⁽⁷⁾. The irradiation time at each stage was $10^{5.5}$ s (~ 88 h), which corresponds to the experiments, and the irradiation temperature was changed stepwisely in the calculation. P , E_m^I and E_m^V were set to be 3.7×10^{-8} dpa/s (average damage rate of the experiment), 0.9 and 1.2 eV[†], respectively, for the present neutron irradiation experiments. Other parameters used in the calculation were estimated on the basis of our previous studies⁽¹⁰⁾⁽¹¹⁾.

1. Defect clustering by increasing irradiation temperature

Change of vacancy and interstitial concentrations under the irradiation at 473 K is shown in Fig. 2(a). Vacancies are accumulated about 10^{-5} by the irradiation for $10^{5.5}$ s. As shown in Fig. 2(b), these vacancies are completely annealed out within 30 s by increasing the temperature to 673 K. If the irradiation is continued even after changing the temperature, the vacancy concentration is kept above 10^{-7} after decreasing about two orders of magnitude by the thermal migration.

The arrival rate of vacancies and interstitials to defect clusters is proportional to their migration efficiencies defined as $M_V C_V$ and $M_I C_I$, respectively. The behavior of the defect clusters depends on which factor is larger. For

Fig. 2 Changes in vacancy and interstitial concentrations under irradiations: (a) irradiation at 473 K; (b) irradiation at 673 K, (a) + irradiation or annealing at 673 K.

example, if $M_I C_I$ is smaller than the $M_V C_V$, vacancy clusters grow but interstitial clusters shrink. Figure 3 shows the changes in migration efficiencies $M_I C_I$ and $M_V C_V$ for the 473/673 K-irradiation and the 673 K-irradiation as a function of the irradiation time at 673 K. In the latter case, $M_I C_I$ is always larger than $M_V C_V$. While in the former case, $M_V C_V$ exceeds $M_I C_I$ temporarily and it should be equal to $M_I C_I$ after irradiation for $10^{5.5}$ s. It can be expected that clusters of vacancies will grow in this period but those of interstitials will shrink. Free vacancies are supplied by two sources, one is the displacement damage, the other is the decomposition of tiny vacancy clusters formed at the low temperature by absorbing the interstitials produced at the high temperature. Figure 4 shows the ratio of the vacancy emitted from divacancy-interstitial reaction with rate of $Z_{2VI} M_I C_I C_{2V}$ to the vacancy produced by displacement damage.

Fig. 3 Changes in the migration efficiencies $M_I C_I$ and $M_V C_V$ for the 473/673 K-irradiation and the 673 K-irradiation as a function of the irradiation time at 673 K.

Fig. 4 Ratio of the vacancy emission rate by divacancy-interstitial reaction to the production rate by displacement damage during the irradiation at 673 K.

[†] 1 eV = 1.602×10^{-19} J.

supplied from the reaction of small vacancy clusters with interstitials exceed 30% of those formed by the displacement at the peak (~ 100 s) because of the tiny vacancy clusters with high density produced by the pre-irradiation. Supply of interstitials from the interstitial clusters is negligibly small. The excess supply of vacancies is the main reason for the vacancy-predominant condition ($M_V C_V > M_I C_I$).

Size distribution of vacancy clusters at several irradiation stages is plotted in Fig. 5. By the irradiation for $10^{5.5}$ s at 473 K, single vacancies as well as small size clusters (mostly divacancies and tri-vacancies) were accumulated in the matrix (the curve (a)). The accumulated single vacancies migrate quickly and form larger clusters by increasing the temperature to 673 K. This clustering process is completed within about 10 s (the curve (b)). After this stage, large re-clustering of vacancies occurs by absorbing radiation induced interstitials and vacancies; concentrations of large clusters increase as shown in curve (c). Curve (d) shows size distribution of vacancy clusters formed by the 673 K-irradiation. Comparison of curves (c) and (d) indicates that the size and amount of small vacancy clusters formed by the 473/673 K-irradiation are large.

Size distribution of interstitial clusters at several irradiation stages is plotted in Fig. 6. It is clear that interstitial loops formed by the pre-irradiation at 473 K shrink considerably by absorbing excess vacancies and most of them disappear after irradiation at 673 K for $10^{5.5}$ s.

2. Defect clustering by decreasing irradiation temperature

The clustering process of defects by decreasing irradiation temperature is discussed in this section. Figure 7 shows the changes of point defect and interstitial loop concentrations during the second 473 K-irradiation following the first 473/673 K cycle irradiation. Those of the first 473 K-irradiation are also shown for comparison. In the case of the second 473 K-irradiation, the change of point defect concentration can be divided into three stages. At the beginning of the irradiation ($t < 1$ s, named stage I), the concentration of interstitials and vacancies formed by the first cycle irradiation is higher than that of the first 473 K-irradiation. With increasing irradiation time ($1 \text{ s} < t < 10^5 \text{ s}$, named stage II), the vacancy concentration is higher than that of the first 473 K-irradiation, but the interstitial concentration is lower, because the accumulated dense vacancy clusters act as sources for vacancies and act as sinks for interstitials. But when the irradiation time is greater than 10^5 s (named stage III), the behavior of interstitials and vacancies formed by the second 473 K-irradiation is contrary to that at stage II, i.e. the vacancy and interstitial concentrations are lower and higher than that of the first 473 K-irradiation, respectively. The interstitial concentration increases due to the suppression of new interstitial cluster nucleation in the second 473 K-irradiation period as shown in the same figure, and vacancy concentration decreases by the recombination of interstitials and vacancies.

Fig. 5 Size distribution of vacancy clusters at several irradiation stages. (a) irradiated for $10^{5.5}$ s at 473 K; (b), (a) + irradiated for 10 s at 673 K; (c), (a) + irradiated for $10^{5.5}$ s at 673 K; (d) irradiated for $10^{5.5}$ s at 673 K.

Fig. 6 Size distribution of interstitial clusters at several irradiation stages. (a) irradiated for $10^{5.5}$ s at 473 K; (b), (a) + irradiated for 10 s at 673 K; (c), (a) + irradiated for $10^{5.5}$ s at 673 K; (d) irradiated for $10^{5.5}$ s at 673 K.

Fig. 7 Changes in vacancy and interstitial concentrations during the first 473 K-irradiation and the second 473 K-irradiation following the first 473/673 K cycle irradiation.

Fig. 8 Changes in migration efficiencies $M_I C_I$ and $M_V C_V$ as a function of the second 473 K-irradiation time.

The migration efficiencies of vacancies and interstitials are plotted in Fig. 8 as a function of the second 473 K-irradiation time. Due to the low mobility of vacancies, $M_I C_I$ is always higher than $M_V C_V$. Namely, interstitial clusters grow but vacancy clusters shrink under the second 473 K-irradiation.

Figures 9 and 10 show size distribution of interstitials and vacancies at the several stages during the second 473 K-irradiation, respectively. Because the migration efficiency of an interstitial is larger than that of a vacancy at all times, interstitial loops grow monotonically. Comparison with nucleation of loops formed by the first 473 K-irradiation is shown in Fig. 6, however, it is clear that the number of the loops nucleated in the second-cycle is much lower. Vacancy clusters, on the other hand, shrink step by step and their size is smaller than that of the first 473 K-irradiation.

3. Comparison with the experimental results of JMTR

The present numerical calculations demonstrate that interstitial clusters shrink but vacancy clusters grow temporarily by increasing the irradiation temperature from 473 to 673 K, because a vacancy-predominant condition is established by the reaction of free interstitials with small vacancy clusters. On the other hand, interstitial clusters grow by decreasing the irradiation temperature, but additional nucleation of interstitial clusters is suppressed by the sink effect of the accumulated vacancy clusters. These theoretical results agree well qualitatively with the experimental results of cyclic temperature irradiation of Fe-Cr-Ni alloy; suppression of interstitial loop and void nucleation⁽⁷⁾.

The rate theory model considered in this work assumes that point defects are produced uniformly and their clusters are formed by thermal migration. In the case of energetic neutron irradiation, however, small vacancy clusters can be directly formed at cascade depleted

Fig. 9 Size distribution of interstitial clusters at several irradiation stages during the second 473 K-irradiation.

Fig. 10 Size distribution of vacancy clusters at several irradiation stages during the second 473 K-irradiation.

zones⁽¹²⁾. It is expected that the amount of tiny vacancy clusters may be higher than that in the present calculation, therefore, more prominent vacancy-predominant condition will be established in the neutron irradiation with increasing temperature.

IV. Summary

In the present study, the effect of the temperature variation on defect cluster processes was analyzed by the rate theory. The numerical calculations show that vacancy-predominant condition appears after changing the temperature from low to high due to the decomposition of small vacancy clusters formed by the low temperature irradiation through the reactions with interstitials produced by the high temperature irradiation. On the other hand, the interstitial-predominant condition is held during the period of changing the temperature from high to low. The excess of interstitials and vacancies formed

during the varying temperature irradiation will suppress or enhance the formation and the growth of interstitial and vacancy clusters.

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