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Effect of solute concentration on grain boundary migration with segregation in stainless steel and model alloys

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Abstract

The phenomenon of grain boundary migration due to boundary diffusion via vacancies is a well-known process for recrystallization and grain growth during annealing. This phenomenon is known as diffusion-induced grain boundary migration (DIGM) and has been recognized in various binary systems. On the other hand, grain boundary migration often occurs under irradiation. Furthermore, such radiation-induced grain boundary migration (RIGM) gives rise to solute segregation. In order to investigate the RIGM mechanism and the interaction between solutes and point defects during the migration, stainless steel and Ni–Si model alloys were electron-irradiated using a HVEM. RIGM was often observed in stainless steels during irradiation. The migration rate of boundary varied, and three stages of the migration were recognized. At lower temperatures, incubation periods up to the occurrence of the boundary migration were observed prior to first stage. These behaviors were recognized particularly for lower solute containing alloys. From the relation between the migration rates at stage I and inverse temperatures, activation energies for the boundary migration were estimated. In comparison to the activation energy without irradiation, these values were very low. This suggests that the RIGM is caused by the flow of mixed-dumbbells toward the grain boundary. The interaction between solute and point defects and the effective defect concentration generating segregation will be discussed.

1. Introduction

Under irradiation, solute redistribution in a concentrated alloy occurs because of the preferential interaction between the solute atoms and the super-saturated point defects moving toward sinks, such as surfaces or grain boundaries. The grain boundary migration phenomenon is generally a well-known process for recrystallization and grain growth during annealing. It is caused by diffusion via vacancies. Diffusion-induced grain boundary migration (DIGM) has been recognized in various binary systems [1–10]. On the other hand, under irradiation environments such as in light water and fast breeder reactors, the boundary migration often occurs even at lower temperatures where no grain boundary movement under thermal annealing would be expected. Furthermore, it has been found that solute redistribution simultaneously occurs at the grain boundary region [11,12].

The radiation-induced grain boundary migration and solute segregation result in significant deleterious effects on the physical, chemical and/or mechanical properties of alloys because of the change of grain boundary characteristics. It is thus of great importance to investigate the mechanism for retardation of the radiation-induced solute redistribution and the behavior of concurrent grain boundary migration under irradiation.

In this paper, the grain boundary migration phenomenon and segregation of solute atoms were studied by in situ observation under electron irradiation for 316L stainless steel and Ni–Si model alloys.

2. Experimental procedures

The specimens used in the present study were 316L stainless steel of Fe–14 wt% Ni–18 wt% Cr–(0.35 at.% Ti, Zr, V, Hf, Nb, or Ta), Ni–1 wt% Si, Ni–3 wt% Si and

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Ni–5 wt% Si. Heat treatments of the alloys were carried out at 1173 K for 30 min and were water quenched. The mean grain size obtained after the recrystallization was about 10 μm. Thin foils were prepared from the specimens by jet electro-polishing (Tenupol), and then were irradiated at 1000 kV to 6.0 dpa in the temperature range of 573–773 K at a mean damage rate of 2.0×10^{-3} dpa/s using a high voltage electron microscope (HVEM). The grain orientations irradiated were typically, ⟨1 0 0⟩, ⟨1 1 0⟩, ⟨1 1 2⟩, and ⟨1 2 2⟩. The distances of grain boundary migration and crystal orientations of grain for irradiation were identified from the micrographs.

3. Experimental results

3.1. Structures under irradiation

Fig. 1 shows the structures observed during irradiation of Ni–1 wt% Si and Ni–5 wt% Si alloys. The grain boundary migration observed in Fig. 1 shows that the migration distance in Ni–5 wt% Si alloy at a given irradiation condition was larger than that in Ni–1 wt% Si alloy.

3.2. Comparison of the candidate stainless steel and the model alloys

Figs. 2 and 3 show the dose dependence of grain boundary migration in the SUS316L stainless steel and the Ni–3 wt% Si model alloy, respectively. Generally, grain boundary migration in general tended to be enhanced at higher temperatures in both stainless steels and model alloys. As will be described later, the migration rate of grain boundaries changed during irradiation. A high density of voids were nucleated during irradiation of SUS316L stainless steel. However, no voids were formed in Ni–Si.

3.3. Temperature and solute concentration dependence of grain boundary migration in model alloys

Figs. 3 and 4 show, respectively, the effect of irradiation temperature and Si concentration on grain boundary migration during irradiation. The curves of grain boundary migration changed with irradiation, and three stages of the boundary migration were obviously recognized: initially there was rapid migration at a first stage of irradiation but during further irradiation the migration rate slowed down (second stage), followed by boundary movement again at a high rate (third stage).

At lower irradiation temperatures, the second stage tended to be longer and an incubation period was also observed prior to first stage. Fig. 5 shows the relation between the migration rates in the first stage and the inverse irradiation temperature. The activation energies for migration of Ni–1 wt% Si, Ni–3 wt% Si and Ni–5 wt% Si alloys were 0.46, 0.29 and 0.17 eV, respectively. Thus, the activation energies decreased with an increase in Si concentration.

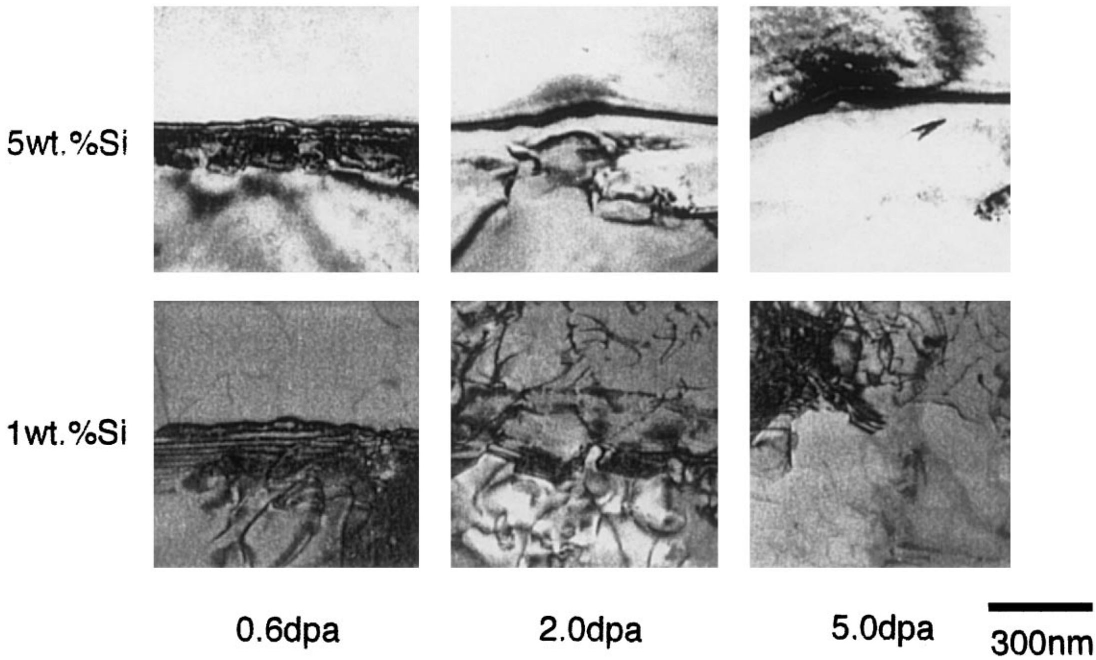

Fig. 1. Microstructural changes and grain boundary migration at 773 K.

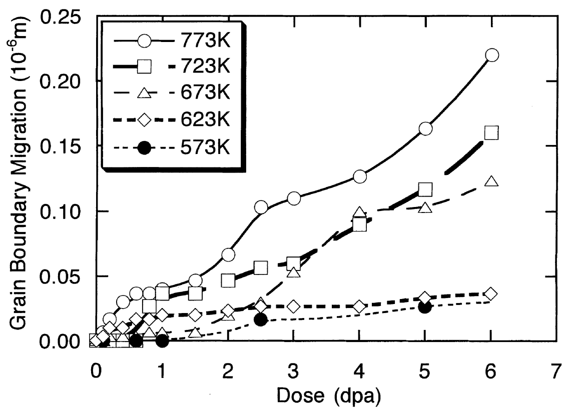

Fig. 2. Dose dependence of boundary migration at 573–773 K in SUS316L stainless steel.

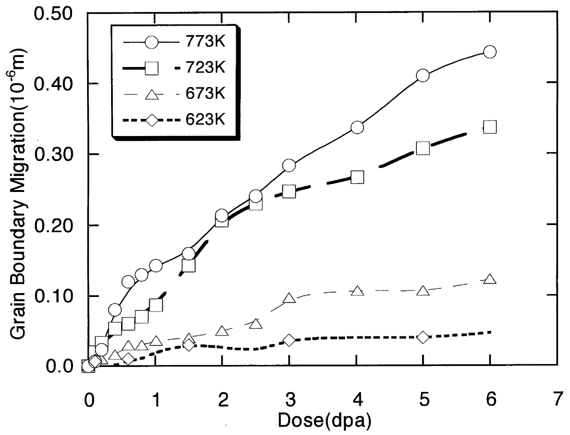

Fig. 3. Dose dependence of boundary migration at 623–773 K in Ni–3 wt% Si alloy.

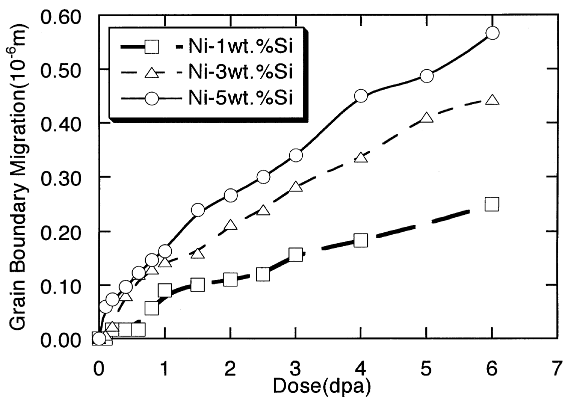

Fig. 4. Si concentration dependence of boundary migration at 773 K.

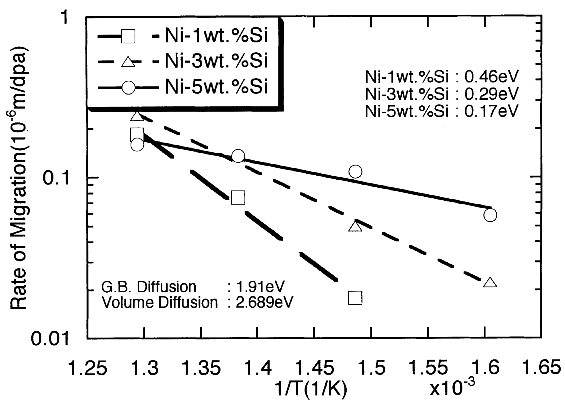

Fig. 5. Temperature dependence of migration rate in Ni–Si alloys (stage I).

4. Discussion

As shown in Figs. 2 and 3, grain boundary migration depended on irradiation temperature in both the 316L stainless steel and the Ni–3 wt% Si model alloy. The same tendency of temperature dependence was recognized for all the model alloys. However, only in 316L stainless steel were voids formed after irradiation to 3 dpa. There is a possibility that due to the formation of voids, the defect flow toward boundary sinks was changed. However, when the grain boundary migration occurs at the early stage of irradiation before void formation, the influence of the voids is negligible.

The activation energies were estimated from the slope in Fig. 5. The values compared to those without irradiation were very low [13]. This suggests that the grain boundary migration under irradiation is related to the flow of interstitials rather than vacancies, and the migration rate is closely attributed to the flux of interstitials.

A large number of interstitials and vacancies are introduced during electron-irradiation so that the irradiation-introduced defect concentration is very high compared with thermal equilibrium. Therefore, these excess point defects form defect clusters and/or migrate to defect sink sites such as grain boundaries. Thus, the irradiation-introduced point defects flow toward boundary sinks during irradiation. It is well known that the oversized elements in alloys preferentially interact with vacancies and diffuse through a vacancy mechanism against the vacancy flow so that the solute becomes depleted at the sink site. On the other hand, the undersized elements which migrate by a mixed-dumbbell mechanism [14], diffuse in the same direction as interstitial atoms. Consequently the solutes are enriched at the sinks. In this process, solute redistribution is induced at grain boundaries. As already reported, the solute segregation is induced at grain boundary under irradiation and the segregation behavior is closely related to the solute size effect [11,15]. Ni and Cr elements in stainless steel(Fe–Cr–Ni alloy) are undersized and oversized ones, respectively. A similar size effect was observed in Ni–Si and Ni–Al alloys. Si and Al solutes are undersized and oversized elements in the Ni-based alloy, respectively. Therefore, Si is enriched and Al is depleted at grain boundaries. From the segregation behavior, it is suggested that the grain boundary migration behavior is closely associated with irradiation-induced defect flow, especially interstitial atoms [16]. Si solute atoms form mixed-dumbbell with interstitial atoms and flow into boundary sink sites because the Si is the undersized atom in Ni–Si alloys. Thus, as shown in Fig. 6 [17], the Si solute segregates on grain boundaries. When the interface of the grain boundary is composed of coarser and denser lattice planes, then the arriving atoms are preferentially rearranged to grow denser boundary planes. Thus, the grain boundary moves as in epitaxial growth by consuming coarser lattice planes.

As explained schematically in Fig. 6, vacancies and interstitial atoms flow into the boundary. When the grain boundary has a large directional difference between two grains [17], the interstitials and solute arriving via mixed-dumbbells are rearranged on denser planes in the interface. One interfacial plane of the grain boundary is newly formed; then, the grain boundary starts to move. This corresponds to the incubation period. Furthermore, the rate of grain boundary migration depends on the rate of rearrangement of interstitials and undersized solutes. This stage corresponds to stage I. In these stages, solute segregation also occurs. As a result, solute concentrations in the vicinity of a migrating boundary away from the boundary interface is lowered because solute atoms in the region diffuse rapidly toward the grain boundary. Furthermore, when interstitial type

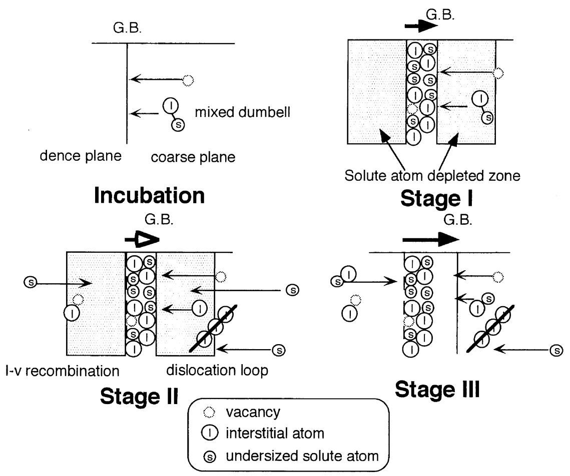

Fig. 6. Schematic description of the stage process in grain boundary migration.

dislocation loops are formed, the rate of grain boundary migration is retarded because some part of interstitials are absorbed at the dislocations. This corresponds to stage II. On the other hand, during stage II, solute atoms diffuse again into solute depleted regions from the neighboring region with higher solute concentration. When the solute concentration of the solute depleted region formed in front of the migrating boundary again reaches the same level as the matrix concentration, the grain boundary migrates with a higher rate, as in stage I. This corresponds to stage III.

In Fig. 4, it is obvious that the alloy with a higher solute concentration causes larger boundary migration at a given dose. Furthermore, it is indicated that the incubation dose becomes shorter for alloys with a high solute concentration. These facts suggest that a critical flux of solute causing the boundary migration becomes also high in alloys with high solute concentrations. Therefore, the time for rearrangement of atoms on the migrating interfacial plane become shorter, so that the incubation dose to start the migration is shorter. Since the boundary migration is closely related to interstitial flow, the activation energy controlling boundary migration depends on that of interstitials. Therefore, the activation energy obtained reflects that for interstitials. From these facts, the role of interstitial atom flow through mixed-dumbbell mechanisms which accompany the solute segregation is more important for boundary migration under irradiation.

5. Conclusions

In this study, electron irradiations were performed for grain boundary regions in SUS316L stainless steel and Si diluted Ni–Si alloys. The results obtained are as follows:

1. There were similar behaviors of grain boundary migration in the SUS316L stainless steel and the Ni–Si model alloys.
2. Grain boundary migration distances showed a marked increase with a rise in irradiation temperature.
3. Grain boundary migration rates varied according to three regions after an incubation period.
4. The apparent activation energy for grain boundary migration obtained at the interfacial first stage corresponds closely to that for the migration of interstitial atoms.

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