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RADIATION-INDUCED MICROSTRUCTURAL CHANGES IN Ni-C AND Pt-C ALLOYS*

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Radiation-induced microstructural changes in Ni-C and Pt-C alloys

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Microstructural changes in Ni-C and Pt-C alloys under irradiation inside a high-voltage electron microscope were investigated as a function of energy and temperature. Two main aspects of microstructural damage by electron irradiation at energies below the displacement threshold of the host elements are discussed: direct displacement of light C solutes by the incident electrons and indirect displacement of heavy Ni and Pt atoms by secondary C-solvent atom collisions. The present study provides new insights into the mechanisms that lead to the formation of defect aggregates in interstitial alloys during sub-threshold energy irradiation.

INTRODUCTION

1. Despite the importance of a basic understanding of the role of interstitial impurities in modifying the swelling behavior of irradiated metals and alloys, information about radiation-induced microstructural instability of alloys containing interstitial solutes, i.e., interstitial alloys, is rather limited. To obtain such information, we have investigated various aspects of microstructural changes in model systems, such as Ni-C and Pt-C alloys, under irradiation inside a high-voltage electron microscope. Owing to the large difference between atomic masses of the alloying elements, interstitial alloys provide a possibility for studying the effects of various damage processes at sub-threshold energies. In fact, in a direct collision, the electrons can transfer 3.4 and 16.3 times more energy to C than to Ni and Pt atoms, respectively; and consequently, Ni and Pt atoms can receive respectively as much as 2.8 and 3.6 times more energy from a secondary collision with energetic C atoms than from a direct collision with electrons. Considering the lowest displacement threshold energies for Ni [21 eV at room temperature (ref. 1)] and for Pt [~35 eV at 4.2 K (ref. 2) and probably just a little less at room temperature] we can readily see that Ni and Pt atoms cannot be displaced by direct collisions with electrons of energies below 0.4 MeV and 1.3 MeV, respectively, near or above room temperature. Hence, in a Pt-C alloy, for example, under 1-MeV electron irradiation, only direct displacement of C atoms and indirect displacement of Pt solvent atoms are expected to take place. Both damage processes generate nonequilibrium point defects, which may cluster after a certain incubation time. As a result, significant changes in the alloy microstructure occur, some of which are highlighted in the present paper. For more details on the starting materials and experimental procedure, the reader is referred to previous communications (refs. 3, 4).

DIRECT DISPLACEMENT OF C SOLUTE ATOMS

2. To study the direct displacement of C atoms by electrons at sub-threshold energies, we irradiated thin films of a quenched Pt-C alloy, in which monolayer {100} C platelets were precipitated by a co-precipitation of C atoms and vacancies (refs. 4,5), and monitored radiation-induced microstructural changes inside these precipitates. It should be pointed out that, in these platelets, C atoms occupy "pseudo-substitutional" sites, as confirmed by transmission-electron-microscopy (TEM) analysis (ref. 5). In as-quenched Pt-C alloys, the precipitates exhibit a well-defined stacking fault contrast with a displacement vector $\mathbf{b} \sim 0.3a\langle 100 \rangle$. During irradiation with electrons of sufficient energy, this contrast is progressively altered by the appearance of black dots inside the precipitates after a certain incubation dose. As the irradiation prolongs, these black dots grow into dislocation loops, and the contrast becomes severely perturbed, as shown in Fig. 1. Detailed TEM analysis has unambiguously indicated that most of these loops were not co-planar with the precipitates; however, no consistent Burgers vector assignment could be made. The present observations can be interpreted as follows. During irradiation, the electrons knock the C atoms out of the precipitates, leaving relaxed vacancies behind in the platelets. These defects subsequently agglomerate into vacancy clusters, giving rise to the observed black dots. Continuing removal of C atoms leads to growth of small vacancy clusters into unstable vacancy loops lying on {100} planes, which finally unfault into an observed complex structure (see ref. 4). The incubation electron dose for the first appearance of black dots inside the C platelets at 400 keV was measured to be $\sim 0.24 \text{ e/cm}^2$. At higher energies, the evolution of the precipitate microstructure was faster, and the incubation doses were smaller, as illustrated by the open squares in Fig. 2.

3. Assuming that the first clusters appear in the platelets at the same critical damage dose, regardless of the electron energy, we can, to a first approximation, express the corresponding electron incubation dose (per unit area), D_e , as a function of incident electron energy, E_0 , and threshold energy, E' , above which the electrons can displace C atoms out of the precipitates (ref. 4). By fitting the so-derived expression to the experimental measurements, we obtained the curve a in Fig. 2 and the threshold voltage $E' = 380$ keV, from which a threshold displacement energy of $E_d = 95$ eV was estimated for C atoms in the platelets. This value is considerably larger than the threshold energies of ~ 35 eV and, a fortiori, ~ 25 eV for atomic displacement in pure Pt (ref. 2) and graphite or diamond (ref. 6), respectively. In our opinion, this high threshold may reflect the fact that, to be permanently displaced, C atoms must be directly ejected into distant interstices, a process requiring considerably more energy than the usual replacement-collision sequence.

4. The spatial distribution of vacancy dislocation loops inside the precipitates that intersected the entrance surface of the foil was not uniform, i.e., there was a dislocation loop-denuded zone in the vicinity of the upper surface when the electron energies were ≥ 700 keV. The occurrence of this zone was understood in terms of recoil implantation of C atoms. Due to thermal segregation, a few C-rich atom layers are unavoidably present at the sample surfaces. Hence, during irradiation, those C atoms that are located on the upper surface are recoil-implanted and pushed downwards into the foil. Owing to a strong vacancy-C interaction, they can fill in the carbon-depleted sites inside the region of the precipitates near the surface, resulting in a transient defect-free zone in the upper-surface region. A decrease in the voltage reduces the range of recoil-implanted C atoms and, hence, reduces the width of the denuded zone. At 600 keV, for example, this denuded zone becomes so thin that it is no longer observable.

5. In addition, increasing the temperature from room temperature to 300°C led to the formation of less numerous, but larger vacancy loops inside the precipitates, as expected from the thermal activation of the vacancy mobility. At a higher temperature, $\sim 400^\circ\text{C}$, vacancy loops were only observed in the peripheral regions of the precipitates because these regions are preferential absorption sites for vacancies. Above $\sim 500^\circ\text{C}$, thermal resolution of the platelets took place, and no difference could be observed between the irradiated and unirradiated regions.

6. Direct displacement of C atoms in Ni-C alloys could not be demonstrated, due to the difficulty in forming C precipitates in these alloys. Several attempts to produce C platelets in Ni containing 0.1, 1, 2, and 8 at.% C were made, but the effort was unsuccessful thus far.

INDIRECT DISPLACEMENT OF HEAVY SOLVENT ATOMS

7. Indirect displacement of the heavy solvent atoms could be observed in both Pt-C and Ni-C alloys. In Pt-C alloys irradiated at room temperature with electrons of energy >600 keV, it was found that, some time after the formation of vacancy clusters inside the damaged precipitates, a number of black dots appeared, multiplied, and grew rapidly into dislocation loops in the matrix (Fig. 3). Stereo electron microscopy revealed that these dislocation loops were uniformly distributed throughout the irradiated region. Their number density increased with the foil thickness, indicating that they were not generated by the agglomeration of vacancies injected by sub-threshold collisions from the bottom surface of the specimen (ref. 7). Furthermore, similar defect clusters were not observed in pure Pt foils irradiated with 1-MeV electrons to a dose as large as 4×10^{23} e/cm². Standard TEM contrast analysis indicated that these dislocation loops were neither vacancy loops nor $\{100\}$ precipitates, but $\{111\}$ interstitial Frank loops. The interstitial nature of the dislocation loops formed is consistent with the reported mobilities of self-interstitials and vacancies in pure Pt. In fact, with a migration energy of ~ 1.40 eV (ref. 8), vacancies are practically immobile at room temperature and can hardly agglomerate into very small clusters. Conversely, with a migration energy of only 0.06 eV (ref. 9), self-interstitials are highly mobile at room temperature and can therefore cluster into large dislocation loops as observed.

8. The incubation dose for the appearance of clusters in the matrix was $\sim 0.3 \times 10^{23}$ e/cm² for 1-MeV electron irradiation. This dose was found to increase with decreasing energy, as shown by the circles in Fig. 2, and to be practically insensitive to the crystallographic orientations for energies used between 0.8 and 1.0 MeV. Assuming again that the first interstitial cluster appears in the matrix at a specific critical damage dose (different from that in the direct displacement case), regardless of the electron energy, we derived another analytical expression for the electron incubation dose as a function of incident electron energy, E_0 , and threshold electron energy, E'' , for displacement of Pt atoms via secondary C-Pt collisions (ref. 4). A fit of this expression to the experimental data yielded the curve b in Fig. 2 and $E'' = 560$ keV, from which a displacement threshold energy of ~ 34 eV was estimated for Pt, consistent with the value measured experimentally (ref. 2).

9. At large irradiation doses, the growing dislocation loops intersect one another and form a dense dislocation network. In addition, at this stage, a number of precipitate platelets in the irradiated area disappear completely. At higher temperatures, interstitial clusters appear at shorter irradiation times, but in lower number density.

10. The observations of indirect displacements in Ni-C alloys were limited to the energy range 300-400 keV; the lower limit, 300 keV, is the lowest energy at which the microscope can be operated without a complete realignment of the column, and the upper limit, 400 keV, is the threshold energy at which Ni atoms can be directly displaced by the incident electrons. Thin films of Ni-1 at.% C alloys were irradiated at 300, 350 and 400°C, near the [011] and [111] crystallographic directions. It should be noted that both the C content and temperature were higher than those in the Pt-C case. Nevertheless, as before, after a certain incubation dose, black dots appeared in the homogeneous matrix (Fig. 4) and progressively grew into faulted dislocation loops. At the time the present paper is being written, the exact nature of these loops has not yet been unambiguously determined; however, it is strongly suspected that they are the usual interstitial Frank loops.

11. The energy dependence of the above incubation dose is shown in Fig. 5 for various temperatures and specimen orientations, θ . For a given orientation, the incubation dose decreases with increasing temperature. On the other hand, at a given temperature, the incubation dose is smaller for [011] than for [111] orientation. By fitting the above-mentioned analytical expression to these data, we obtained $E^* = 245$ keV and a displacement threshold energy of ~ 31 eV for Ni, regardless of orientation and temperature. The latter value is in satisfactory accord with the published measurements (ref. 1). In addition, from the value of E^* , we deduced a minimum energy of $U^* = 104$ eV that must be transferred to C atoms so that they can displace Ni atoms by secondary collisions.

12. In contrast to the Pt-C case, at lower temperatures, $< 280^\circ\text{C}$, no clearly-resolved clusters could be observed, even after very long exposures to irradiation. The irradiated area simply became darker and darker with increasing dose, indicating that some kind of microstructural changes occurred on a fine scale. A question is now raised: if defect clusters formed in the matrix were of an interstitial nature, why couldn't we resolve them at room temperature as in the previous case of Pt-C alloys? This leads us to speculate that there may be a strong interaction between self-interstitials and C atoms in Ni-C alloys; below $\sim 280^\circ\text{C}$, the effective mobility of the interstitial is rather sluggish, and only above this temperature, interstitial-C complexes dissociate and free interstitials can migrate over long distances. This aspect is the subject of continuing studies.

13. That light solutes can produce sub-threshold knock-ons in an indirect fashion was first suggested by Nabner and James (ref. 10) after their observations of damage at very low energies in Ge containing H atoms. Subsequently, the effects were also observed in other metals, such as Al (ref. 11), Au (ref. 12), and

Cu (refs. 12,13), in which light-atom impurities were present, either by doping or because of unavoidable contamination. The most striking point is certainly that only small additions of light elements are sufficient to produce numerous interstitial clusters under sub-threshold irradiation. This probably happens because the cross sections may be very large for secondary displacement.

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Fig. 1. Formation of dislocation loops inside the C precipitates during 600-keV electron irradiation at room temperature to a dose of 3.4×10^{23} e/cm². $\hat{n} \sim [111]$ and $\hat{g} = [02\bar{2}]$.

Fig. 4. Formation of dislocation loops in a Ni-1 at.% C alloy during 350-keV irradiation at 400°C to a dose of $\sim 0.5 \times 10^{23}$ e/cm². $\hat{n} \sim [011]$ and $\hat{g} = [200]$.

Fig. 2. Energy dependence of the incubation doses for the appearance of defect clusters inside the C precipitates (curve a) and in the Pt matrix (curve b) of a Pt-0.1 at.% C alloy.

Fig. 3. Microstructure of an as-quenched Pt-C alloy after 1-MeV electron irradiation at room temperature to a dose of 9.8×10^{23} e/cm². $\hat{n} \sim [011]$ and $\hat{g} = [200]$.

Fig. 5. Energy dependence of the incubation dose for the appearance of defect clusters in a Ni-1 at.% C alloy irradiated at various orientations and temperatures: (★) $\hat{n} \sim [111]$, 300°C; (●) $\hat{n} \sim [111]$, 350°C; (■) $\hat{n} \sim [111]$, 400°C; (○) $\hat{n} \sim [011]$, 350°C.