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# Effect of phosphorus on vacancy-type defect behaviour in electron-irradiated Ni studied by positron annihilation

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ABSTRACT

Very dilute Ni–P system (containing 50–240 appm phosphorus) irradiated by 5 MeV electrons at various temperatures (270–543 K) was studied by positron annihilation spectroscopy (PAS) and the electrical resistivity measurements. Under irradiation at 270 K (below stage III in Ni), the accumulation of the monovacancies in the Ni–P system is 1.5–2.0 times greater than that in pure Ni irradiated in the same conditions. This fact attests to the strong interaction between P atoms and self-interstitial atoms (SIAs). As a result of the non-mobile SIA–P complexes formation, the mutual recombination of point defects is suppressed and the vacancy accumulation is, respectively, enhanced. During post-irradiation annealing, the vacancy migration induces the transport process of the phosphorus atoms and leads to the formation of the vacancy clusters decorated with P atoms. The annealing behaviour of the defect structures in Ni–P systems after irradiation at enhanced temperatures was also studied. The influence of phosphorus on the formation and further evolution of the vacancy aggregates decrease with increasing of the irradiation temperature.



## 1. Introduction

The point defects such as vacancies and self-interstitial atoms (SIAs) are produced in metals under high-energy particle irradiation. The diffusion of these defects cases fine microstructural changes in metals that lead to modification in their physical–mechanical properties. The diffusion of vacancies is of interest because the vacancies not only form clusters, voids and/or loops but also promote the diffusion of substitution-type solute atoms in the matrix. The diffusion of solutes via the vacancy mechanism may cause the clustering, segregation and precipitation of the solute atoms. This solute diffusion is controlled by the strength of the interaction between a vacancy and the solute atom, whose magnitude depends on the element. First-principles calculations of the vacancy-3sp-element interactions in bcc Fe were conducted in [1,2]. It was shown that, in the case of important technologically 3sp-elements (Si, P, S), the binding energy is approximately 0.3–0.5 eV. Hence, under irradiated conditions, vacancies should drag 3sp-atoms (in particular P atoms) towards sinks of point defects in bcc Fe [3].

The previous studies showed, in particular, that the phosphorus addition to austenitic stainless steels (SS) has a significant effect on suppressing of void swelling [4]. The suppression can be explained by an enhanced loop formation due to an interaction of P with vacancies and/or SIAs [5]. In addition, the formation of phosphide precipitates is thought to enhance the point defect recombination at the precipitate–matrix interfaces [6]. On the other hand, it is known that phosphorus atoms (as sulphur) segregate to grain boundaries (GBs) in reactor structural materials (SS, pressure vessel steels) under irradiation and have detrimental effects on their physical and mechanical properties. In particular, this leads to a decrease in the grain boundaries cohesion and, consequently, to an increase of the ductile-to-brittle transition temperature [7]. For this reason, the kinetics of P segregation to GBs in steels and model alloys under irradiation has been studied extensively [8].

As mentioned above, the mechanism of the solute segregation is controlled by the strength of the interaction between point defects and the solute atom, whose magnitude depends on the element [3]. The phosphorus atoms in the Ni solid solution exist as undersized impurities as Si and S [9]. Therefore, P atoms are expected to form bound solute–interstitial pairs, which can migrate over long distances. For example, the authors [10] from the analysis of data on P segregation in Ni consider the migration of phosphorus atoms to sinks via the interstitial mechanism. They also assume that P atoms weakly interact with vacancies in Ni. However, Watanabe et al. [5] suggested that vacancies are trapped by P atoms in austenitic alloys. We have shown earlier [11] that vacancy clusters decorated with P atoms are formed in austenitic Fe–Ni alloys during electron-irradiation at 270 K, but the decoration effect is not

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observed during the irradiation at 423 K. Thus, the generally accepted point of view on mechanisms of the phosphorus migration under irradiation in SS and Ni-base alloys is absent today.

The objective of the present study is to investigate the effect of the phosphorus addition on the radiation-induced defect evolution in pure Ni. Nickel is studied because it is a major alloying element in austenitic stainless steels and Ni-base alloys used in nuclear engineering. The Ni–P system has been irradiated by 5 MeV electrons at 270 K (before onset of stage III) and also at enhanced temperatures (473 and 543 K) to introduce SIAs and monovacancies. The defect–phosphorus interaction has been studied by using positron annihilation method.

Positron annihilation technique has become a powerful tool for investigation of vacancy-type defects in metals and alloys [12]. Since positively charged nuclei are absent at vacancy-type defects, positrons are trapped and annihilate there with the surrounding electrons, conveying the information on the local electronic environment around the vacancy-type defects. Coincidence Doppler broadening [13] and angular correlation of annihilation radiation (ACAR) [14] enables us to identify the chemical element whose electron annihilate with the positron, by measuring the electron momentum distribution in the high-momentum region, given by the positron annihilation with the core electrons. It can identify the chemical environment of the annihilation site, because the core electrons are tightly bound to the nuclei and almost unaffected by crystal structure. Thus, those methods can probe the formation both vacancy-type defects, with sensitivity starting from the atomic size to large vacancy clusters and nanovoids [12], and the vacancy–solute complexes [13,14], whereas they are insensitive to interstitial atoms and their small agglomerates. However, the accumulation and annealing kinetics of the vacancy-type defects may be affected not only by the interaction of vacancies with solute atoms, but also by rearrangements of the SIA–solute atom complexes formed during irradiation.

In the present work, attempts have been made to clarify the fundamental aspects of the interaction between phosphorus atoms and irradiation-induced defects by means of the ACAR and residual electrical resistivity (RR) measurements. RR reveals a high integral sensitivity to point defects and content of P in solid solution.

## 2. Materials and methods

High-purity Ni single crystals were prepared by the floating-zone-refinement in high-purity hydrogen gas. The samples (from zone-refined Ni) were spark-cut, mechanically thinned and electropolished. To remove possible defects introduced by preparation, the specimens about $10 \times 10$ mm$^2$ in size ($\sim$0.25 mm thick) were annealed at 1270 K in a vacuum of $10^{-5}$ Pa for 4 h and then cooled slowly. The residual resistivity ratio (RRR) 300 K/4.2 K of specimens was about 800. The estimated content of residual impurities was $\sim$10 atomic parts per million (appm). One sample set was utilised in the phosphorus-free experiments, whereas a second set was doped with phosphorus by means of diffusion alloying. The doping was carried at $\sim$1320 K for time periods ranging from 10 h to 100 h with subsequent quenching into water. The mean linear intercept grain size for heat treated Ni–P was $\sim$250 μm. The technique of alloying has been described in detail earlier (see [15] and references therein). The phosphorus concentration in solid solution (matrix) Ni was estimated from the residual resistivity increment. In this study, samples of the Ni-50 appm P and Ni-240 appm P (Ni–P) were used. The samples were quenched into water (quenching rate $\sim$200 K/s) or cold helium ($\sim$80 K/s) after each thermal treatment to keep P atoms in solid solution. Phosphorus is moderately soluble in nickel. For example, the solubility limit of P in Ni is about 0.9 at.% at temperature of 1370 K [16].

In order to check whether the samples may be contaminated with other impurities during alloying, we performed control experiments. They included all of the operations used during diffusion alloying except loading of phosphorus. Comparison of mass-spectrometry and resistivity data obtained on the initially pure Ni and control samples showed no additional contamination of specimens.

The all Ni–P samples were solution annealed in a purified helium atmosphere at 873 K for 1 h and then cooled quickly in water (SA state).

Samples of the Ni and Ni–P system were irradiated at 270 K with 5 MeV electrons in a linear accelerator. In addition, samples of Ni-240 appm P system (in SA state) were irradiated at enhanced temperatures (473 and 543 K). The samples were positioned as tightly as possible in the centre of the irradiation zone ($10 \times 10$ mm$^2$) of the sample holder and the electron beam sweeping was applied to provide homogeneous irradiation. After irradiation to half of the total fluence, the sample holder with the specimens was reversed in order to obtain a symmetric distribution of damage in the samples. The irradiation temperature was controlled to within ±5 K. The maximum electron fluence was $5 \times 10^{22}$ m$^{-2}$. The fluence concerned with damaging dose by:

$$D(E_e) = \phi \sigma^e_{eff}(E_e), \quad (1)$$

where $E_e$ – electron energy, $\phi$ – electron fluence, $\sigma^e_{eff}$ – effective cross-section for displacement of atoms by an electron calculated following the method outlined in [17]. The maximum fluence corresponds to the damaging dose of $\sim 5 \times 10^{-4}$ dpa.

The as-irradiated samples were isochronal (stepwise) annealed (25–50 K per step with a holding time 25–50 min) over the temperature range from 270 to 900 K in a purified helium atmosphere and then rapidly cooled with cold helium.

The residual resistivity of the samples was measured at 4.2 K using an automated measuring setup with an accuracy of 0.05% and a sensitivity of $5 \times 10^{-12}$ Ω cm. The four-probe method employed. For resistivity experiments, strips about 50 μm thick were produced by cold rolling, from which meander-shaped samples were spark-cut (about 0.6 mm in width and 8 mm effective length). Further treatment of samples was the same as those used in the positron annihilation experiments.

The ACAR measurements were performed at RT. This method was realised in a one-dimensional ACAR spectrometer providing a resolution of 1 mrad × 160 mrad [18]. A $^{22}$Na positron source of activity of 400 MBq was used. At least $5 \times 10^5$ coincidence counts were collected in each ACAR spectrum; the peak-to-background ratio was $\sim 10^3$. The ACAR spectra represented the dependence of the coincidence count rate on the angle $\theta$ ($\theta$ being the deviation of the two annihilation gamma-quanta from anticollinearity). The angle $\theta = p_z/m_0c$, where $p_z$ is the transverse component of the momentum of an electron–positron pair to the direction of the emitted gamma-quanta, $m_0$ is the rest mass of an electron, and $c$ is the light velocity. The ACAR data contain information about the momentum distribution of annihilating electrons and it is possible to separate contributions from annihilation of positrons with valence electron (low-momentum part of the spectrum) and core electrons (high-momentum part of the spectrum) [18]. The momentum distribution of core electrons can be used to determine the chemical environment of an annihilation site [13].

The ACAR spectra of the Ni are well represented by the sum of a parabolic contribution from positron annihilation with valence electrons and an essentially Gaussian contribution from annihilation with core electrons [12]. The approximation procedure that takes account of the spectrometer resolution function and background is described in detail elsewhere [18]. The variance of the fit was below 1.2.