Radiation-induced defects in solid solutions and intermetallic compounds based on the Ni–Al system: I. Low-temperature electron-irradiation damage

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Abstract. The effect of alloy composition on radiation damage by 2.95 MeV electrons at low temperature has been investigated in Ni(Al) and Ni(Al,Ti) solid solutions and in Ni_3Al intermetallic compounds (24.6–26.5 at.% Al) by residual electrical resistivity measurements. In the solid solutions the main result of irradiation was point-defect production. Frenkel-pair resistivities, deduced from the comparative analysis of the initial damage rates in the solid solutions and in pure nickel, were 6.5–9.4 $\mu\Omega$ cm/%, similar to or slightly larger than the value of nickel. In Ni_3Al intermetallic compounds, the resistivity damage rates were enhanced by a factor of about 15 compared with pure nickel. Disordering contributes only a small part of this increase. Assuming an average of 3 ± 1 replacements per displacement, a comparison of the initial damage rates in nickel and in the compounds leads to Frenkel-pair resistivities ranging from 97 to 109 $\mu\Omega$ cm/%. Such high values may be correlated with the large ideal resistivity of these materials.

1. Introduction

Aerospace propulsion systems require materials with good structural stability and creep resistance at high temperatures. Nickel-based γ/γ' superalloys are presently used; their strength results from the presence of a hardening γ' phase (an $L1_2$-type intermetallic compound) dispersed in a short-range-ordered FCC nickel-based solid solution. The high-temperature properties are dependent on the atomic mobilities, via vacancy diffusion, in the two phases. Thus the coalescence rate of the precipitates is proportional to the diffusion coefficient in the γ matrix, in the model developed by Lifshitz, Slyozov (1961) and Wagner (1961), as well as in the later improved versions (Voorhees 1985), which take into account the interaction between particles. Furthermore, according to the conditions, the creep rate is mainly controlled by dislocation climb either in the γ phase or in the γ' phase and thus depends on the diffusion rate in the corresponding phase. Therefore, it is essential for a better understanding of the high-temperature behaviour of the superalloys to have information on the vacancy properties in both the γ and the γ' phases.

   Industrial materials contain many constituent elements, the specific effect of which is not clearly understood. Consequently, in the present work, single-phase binary alloys were first investigated; the effect of composition in Ni(Al) and of deviations

from stoichiometry in Ni_3Al compounds were respectively considered. In a second stage, the addition of titanium (which is a constituent of industrial superalloys) to Ni(Al) was studied.

The present work aimed at determining the properties of non-equilibrium vacancies, as well as self-interstitials, produced by electron irradiation at low temperature. Irradiation effects in the Ni–Al system have been little investigated, by contrast with other systems including $L1_2$ phases like Au–Cu (Alamo *et al* 1986, Urban and Ehrhart 1987). γ' precipitation in Ni(Al) alloys, containing 11.1 and 13.1 at.% Al, has been studied under proton irradiation in the 433–633 K range (Jung *et al* 1987). Some results are available in γ' $Ni_{76.3}Al_{23.7}$; they were obtained by positron lifetime measurements in samples irradiated mainly at room temperature (Shimotomai *et al* 1983, Wang *et al* 1984, Doyama *et al* 1987) and at 21 K (Doyama *et al* 1985).

The results will be presented in two parts. Here, in part I, we report and discuss the damage induced at 4–9 K by electron irradiation, in the short-range-ordered alloys $Ni_{94}Al_6$, $Ni_{90}Al_{10}$, $Ni_{96}Al_1Ti_3$ and in long-range-ordered Ni_3Al compounds, with different compositions (24.6–26.5 at.% Al). Radiation damage was investigated by residual electrical resistivity measurements; point-defect production and disordering processes are discussed and we attempt to evaluate the Frenkel-pair resistivity in these materials. Part II (Dimitrov *et al* 1992a) will be devoted to the recovery mechanisms during isochronal anneals at increasing temperatures and to the determination of the mobility of vacancies and self-interstitials.

2. Experimental details

The materials investigated were Ni/6 at.% Al, Ni/10 at.% Al, Ni/1 at.% Al/3 at.% Ti solid solutions (named $Ni_{94}Al_6$, $Ni_{90}Al_{10}$, $Ni_{96}Al_1Ti_3$) and three Ni_3Al intermetallic compounds containing 24.6, 25.0 and 26.5 at.% Al respectively (named $Ni_{75.4}Al_{24.6}$, $Ni_{75.0}Al_{25.0}$ and $Ni_{74.5}Al_{26.5}$). The alloys were prepared by melting together in an inductive plasma furnace weighed amounts of nickel, aluminium and titanium. Pure metals were used to prepare the alloys. Nickel was obtained from ENSM, St Etienne; its residual electrical resistivity ratio (RRR) was $R_{294\ K}/R_{4.2\ K} = 940$. Electrolytic aluminium, purchased from Swiss Aluminium Ltd, Neuhausen, was zone-refined in CECM, France, yielding a material with a bulk resistivity ratio of 21 000. Electrolytic titanium was obtained from Ugine and melted in a water-cooled copper crucible, under a purified argon atmosphere (RRR = 27). The alloy ingots, of 4–5 g in weight, were melted several times; they were then homogenized by annealing for 24 h at 1273 K under a vacuum lower than 10^{-5} Pa, followed by slow furnace cooling. Some weight losses, smaller than 0.1% of the sum of the constituents, occurred during melting. The final compositions are given in tables 1 and 2. For the Ni_3Al compounds, true compositions† were calculated by assuming that mainly nickel was lost as a consequence of the partial vapour pressures of nickel and aluminium determined in $Ni_{75}Al_{25}$ at 1728 K, above its melting point (Bremer 1988).

The alloys were checked to be single phase by x-ray diffraction, lattice parameter determinations, and transmission and scanning electron microscope (TEM, SEM)

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† Slightly different compositions of the off-stoichiometric alloys were previously given: they were determined by using, for the loss corrections, the partial vapour pressures of aluminium and nickel in the pure metals.

Table 1. Compositions, initial resistivities ρ_0 at 4.2 K, experimental initial damage rates $(d\rho/d\Phi)_0$, relative displacement cross sections $\sigma_d^{Ni}/\sigma_d^{alloy}$, Frenkel-pair resistivities ρ_F and extrapolated saturation resistivities $\Delta\rho_s$ of the short-range-ordered alloys.

Materials	Ni	Ni$_{94}$Al$_6$	Ni$_{90}$Al$_{10}$	Ni$_{96}$Al$_1$Ti$_3$
Al (at.%)	0 (pure Ni)	6.0	9.8	1.0 +2.9 at.% Ti
$\rho_0(10^{-6}$ Ω cm)	0.0430 ± 0.0002	12.39 ± 0.06	23.25 ± 0.10	13.71 ± 0.01
$(d\rho/d\Phi)_0$ $(10^{-26}$ Ω cm^3)	2.08 ± 0.04	1.97 ± 0.06	2.55 ± 0.05	2.89 ± 0.10
$\sigma_d^{Ni}/\sigma_d^{alloy}$	1	1.023	1.040	1.010
$\rho_F(\mu\Omega$ cm/%)	6.7	6.5 ± 0.6	8.5 ± 0.8	9.4 ± 1.2
$\Delta\rho_s(\mu\Omega$ cm)	1.4 ± 0.5	2.6 ± 1.1	1.9 ± 0.4	—

metallographic observations. The stability of the FCC γ phase in the Ni$_{90}$Al$_{10}$ alloy was specially investigated, since this composition is near the γ–γ' solubility limit of the phase diagram (Hansen and Anderko 1958, Sanchez *et al* 1984). No γ' precipitates were observed by TEM, in a sample aged for 435 h at 660 K, and no change of the Curie temperature, which is sensitive to the aluminium content of the γ phase, was detected.

Local order in binary Ni(Al) solid solutions has been observed and the Warren–Cowley parameters have been determined by x-ray diffuse scattering measurements (Klaiber *et al* 1987, Chassagne *et al* 1989). Short-range ordering (SRO), induced by appropriate thermal treatments, results in an increase of the electrical resistivity (Afyouni *et al* 1989, Sitaud and Dimitrov 1989).

The L1$_2$ structure characterizing the γ' phase is limited to a narrow composition range around 75 at.% nickel. The three compositions investigated here were found to be single phase, in agreement with the detailed section of the phase diagram analysed by Hilpert *et al* (1987) and Bremer *et al* (1988). The long-range-ordered (LRO) structure is considered to be stable up to the melting point. However, thermal treatments above 780 K were found recently to induce electrical resistivity changes in the alloys and these were assigned to LRO variations (Kozubski and Cadeville 1988, Zhang 1989, Sitaud *et al* 1990); long-range ordering leads to a residual resistivity decrease.

For the preparation of the irradiation specimens, fractions of the solid solution ingots were cold-rolled to a thickness of ~ 30 μm and samples were mechanically cut out from the foils. Pure nickel samples, used as reference in the irradiation experiments, were prepared by the same procedure. The intermetallic compounds displayed intergranular brittleness; therefore, strips of ~ 300 μm in thickness were cut out from the ingots with a diamond saw, then thinned to 130–270 μm by mechanical polishing. After subsequent chemical or electrochemical etching, the samples were annealed in a $\sim 10^{-5}$ Pa vacuum for 30 min at 1273 K (solid solutions) or 10 h at 1173 K (intermetallic compounds) or for 2 h at 1073 K in the case of pure nickel, respectively, then furnace cooled.

Twelve samples were mounted on the irradiation holder. They were irradiated with 2.95 MeV electrons, in a helium flow cryostat (details are given by Schroeder and Schilling (1976)); the electron flux density was $\sim 3 \times 10^{13}$ e cm^{-2} s^{-1} and did not vary across the irradiated sample area by more than $\pm5\%$. The irradiation temperature varied from 4.6 to 9 K as a function of the samples thickness. Sets of

three different materials were simultaneously irradiated in four different runs up to 4.2 and 8.0×10^{18} e cm^{-2}. All the alloys and nickel were irradiated at these two fluences except $Ni_{96}Al_1Ti_3$ and $Ni_{75.4}Al_{24.6}$, which were irradiated only at one fluence.

Radiation damage was investigated by electrical resistivity determinations performed at 4.6 K by standard four-point DC measurements. The shape factors of the alloy samples $k = \rho_{4.2\ K} / R_{4.2\ K}$ were deduced from their electrical resistance (R_0) before irradiation, using the resistivities (ρ_0) given in tables 1 and 2. These were determined on separate specimens of suitable shape, ~ 1 mm^2 in section, annealed in the same conditions as given above. The shape factors of the nickel samples were calculated from the ideal resistivity at 296 K ($\rho_i = 7.04\ \mu\Omega$ cm) and from the electrical resistances measured at this temperature and at 4.2 K by the relationship $k = \rho_i / R_{296} - R_{4.2}$). The uncertainty on resistivity determinations was 1×10^{-9} Ω cm.

3. Results and discussion

The resistivity variations produced by electron irradiation in pure nickel, in the solid solutions and in the intermetallic compounds are given in figures 1(a) and 2(a) as a function of fluence Φ. The curves exhibit qualitatively similar shapes: with increasing Φ the resistivity increases at a progressively slower rate; however, the excess resistivities $\Delta\rho_i$ produced by the same fluence differed considerably between the SRO and the LRO alloys. The values were of the same order in nickel and in the $Ni_{94}Al_6$ alloy, and a little higher in the other solid solutions. By contrast, the radiation-induced resistivities were larger by a factor of ~ 15 in the intermetallic compounds than in pure nickel. The differences observed between the three intermetallic compounds were not significant, taking into account the $\pm5\%$ error in the electron flux homogeneity.
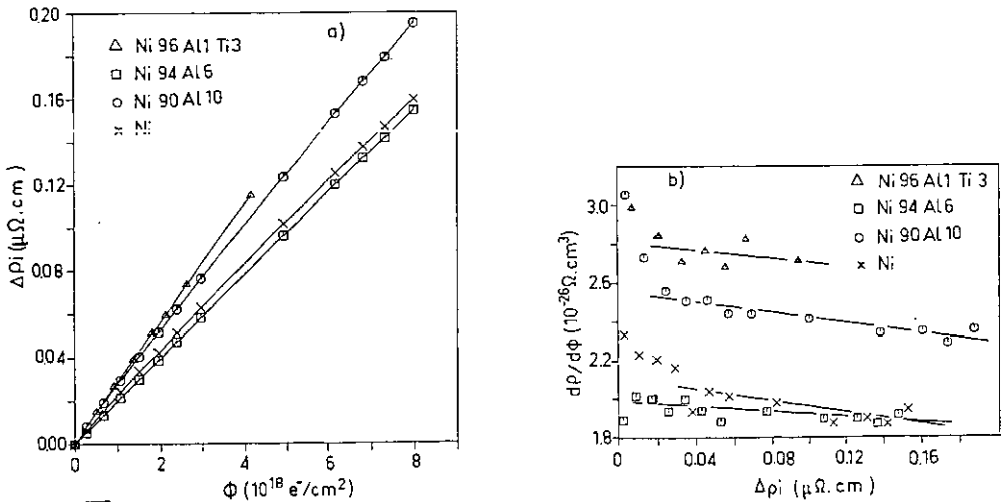

Figure 1. (a) Resistivity variations during electron irradiation at 4.2 K in nickel and in Ni solid solutions (lines are drawn to guide the eye). (b) Resistivity damage rates in the same materials (lines are least-squares fits to equation (1)).
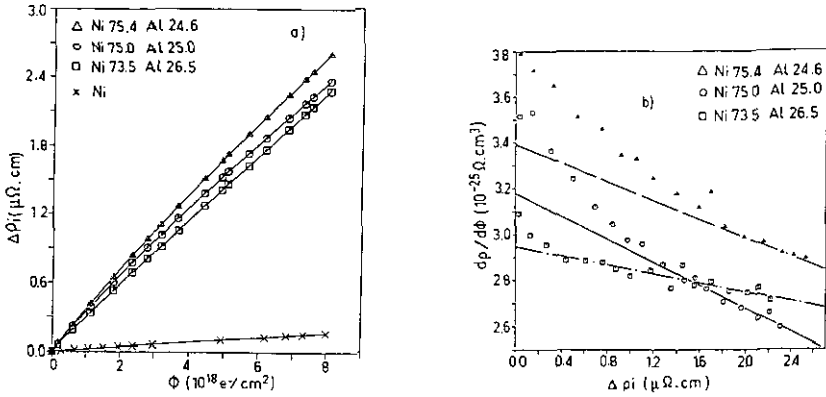
Figure 2. (*a*) Resistivity variations during electron irradiations in Ni$_3$Al alloys and in Ni (lines are drawn to guide the eye). (*b*) Resistivity damage rates in Ni$_3$Al alloys (lines are least-squares fits to equation (1)).

3.1. Resistivity damage rates and Frenkel-pair resistivities in the solid solutions

The resistivity damage rates $d\rho/d\Phi$ were evaluated as a function of the radiation-induced resistivity (figure 1(*b*)). A rapid decrease of the rate was observed at low fluences and appears as a 'tail' in most of the samples; its magnitude depends on the composition of the alloys. The resistivity damage rates determined in the solid solutions and in pure nickel were similar. Thus, we consider that disordering induced by irradiation has a minor influence on the damage as compared to defect production. Furthermore, disordering should lead to a negative contribution to resistivity, more important in the Al-rich alloy Ni$_{90}$Al$_{10}$ since the order resistivity (i.e. the difference between the resistivities of the unirradiated alloy and of the totally disordered material) is three times larger in Ni$_{90}$Al$_{10}$ than in Ni$_{94}$Al$_6$ (Sitaud and Dimitrov 1990). Thus the damage rate should be smaller in the former alloy, in contrast with the experimental results.

The assumption of a negligible disordering contribution to the resistivity variation in the solid solutions is not in contradiction with the estimation of this contribution in the intermetallic compounds. For a given atomic replacement efficiency, the effect of disordering on the resistivity damage rate should be proportional to the order resistivity ($\rho_{\text{disordered}} - \rho_{\text{ordered}}$). This quantity is much larger in the investigated intermetallic compounds, 27 to 36 $\mu\Omega$ cm (see section 3.2.1(i)), than in the solid solutions, 0.4 to 4 $\mu\Omega$ cm (Sitaud 1991), so that the contribution to the resistivity damage rate may be significant in the Ni$_3$Al materials, and not in the solid solutions. Furthermore, the atomic replacements due to replacement sequences may be more effective, in alloys with a mass difference between the constituent atoms, when a long-range-ordered sequence exists in the atomic rows concerned.

After the initial 'tail', the resistivity damage rate curves could be fitted to the equation:

$$\dot{\rho} = d\rho/d\Phi = \sigma_d \rho_F [1 - (2\nu_0 \Delta\rho)/\rho_F] \tag{1}$$

where σ_d is the displacement cross section and ν_0 the vacancy–interstitial recombination volume. Extrapolation of the linear part of the curves gives experimental values of the initial resistivity damage rate $(d\rho/d\Phi)_0$ at $\Delta\rho_i = 0$ and

of the saturation resistivity $\Delta\rho_s$ (corresponding to a damage rate $d\rho/d\Phi$ equal to zero).

An evaluation of the Frenkel-pair resistivity ρ_F by the direct application of equation (1) would require a knowledge of the absolute displacement cross sections. Thus, a relative method was used: the experimental initial resistivity damage rates of the solid solutions (table 1) were compared with the one obtained in nickel, for which ρ_F is well known (Bender and Ehrhart 1983, Dimitrov and Dimitrov 1985), yielding

$$\rho_F^{\text{alloy}} = \rho_F^{\text{Ni}} \left(\dot{\rho}_0^{\text{alloy}}/\dot{\rho}_0^{\text{Ni}}\right) \left(\sigma_d^{\text{Ni}}/\sigma_d^{\text{alloy}}\right). \tag{2}$$

Since the crystallographic structure of nickel and of the solid solutions is the same (FCC), we expect that the uncertainties in the displacement cross section ratios should be reduced by this method.

The displacement cross sections of the nickel-based alloys containing x at.% aluminium (and y at.% titanium in the ternary alloy) were determined by the formula:

$$\sigma_d^{\text{alloy}} = [1 - (x + y)/100]\sigma_d^{\text{Ni}} + (x/100)\sigma_d^{\text{Al}} + (y/100)\sigma_d^{\text{Ti}}. \tag{3}$$

Values of σ_d^{Ni}, σ_d^{Al} and σ_d^{Ti} were calculated from Oen's (1973) tabulation by taking for the three elements the same effective average atomic displacement energy $\hat{E}_d = 69$ eV, as proposed by Jung (1981) for nickel. The results, given in table 1, indicate that the value of ρ_F is not significantly modified in the $\text{Ni}_{94}\text{Al}_6$ alloy; it is increased in the $\text{Ni}_{90}\text{Al}_{10}$ alloy, and a larger effect is observed in the case of the addition of titanium. This evolution in the binary alloys cannot be explained by some disordering induced by irradiation, which has a negative contribution to resistivity, larger in $\text{Ni}_{90}\text{Al}_{10}$ than in $\text{Ni}_{94}\text{Al}_6$ (Sitaud and Dimitrov 1990).

A rough value of the recombination volume ν_0 was estimated from the extrapolated saturation resistivity $\Delta\rho_s$:

$$\nu_0 = \rho_F/2\Delta\rho_s \tag{4}$$

and ν_0 was found equal to ~ 200 atomic volumes in nickel and in the nickel-based alloys. Recombination volume data have not been previously published for electron-irradiated nickel. Values of 184 to 257 atomic volumes have been reported (Jung 1991) for irradiations by light ions (protons and helium ions, in the energy range 0.5–1.5 MeV), which should give a comparable defect structure.

3.2. Resistivity damage rates and Frenkel-pair resistivities in the intermetallic compounds

The resistivity damage rates in the intermetallic compounds were strikingly larger than in pure nickel (figure 2(b)). Disordering, which leads to a resistivity increase, could be effective during electron irradiation. Such disordering was observed in Ni_3Al (Butler and Orchard 1981, Liu and Mitchell 1983). Their samples were irradiated in a high-voltage electron microscope, at low temperatures, down to 10 K, with a high flux density ($\geqslant 1 \times 10^{19}$ e cm^{-2} s^{-1}), larger by a factor $\sim 3 \times 10^5$ than the one used in the present work. In our experiments, it is difficult to separate directly the contribution to resistivity of point defects from that of disordering, since a comparison with data on disordered alloys of the same composition is not available (in Ni_3Al, the order–disorder transition was suggested to take place around the melting temperature

(Cahn *et al* 1987), so that the Ni_3Al compounds remain long-range-ordered up to the melting point).

To analyse the resistivity damage rates, we first evaluate the expected effect of disordering by irradiation. Then, we subtract that contribution from the experimentally determined rate, in order to obtain the defect damage rate and to derive point-defect parameters. Finally, the sensitivity of the results to the underlying assumptions will be checked by considering two extreme limiting cases, i.e. negligible defect resistivity or negligible order resistivity.

3.2.1. Estimation of disordering contributions to radiation damage, and derivation of defect parameters. In long-range-ordered Ni_3Al, disordering results from the formation of antisite defects, produced mainly by atomic replacement collisions. Disordering induced by random interstitial–vacancy recombination can be neglected here, since the probability of such a process is small at the ~ 9 K irradiation temperature, where both interstitials and vacancies are immobile (see part II), and at the low displacement level, which leads to limited spontaneous recombination.

The experimental initial damage rate $(d\rho/d\Phi)_0^{exp}$ was considered as the sum of two contributions: one due to point-defect production $(d\rho/d\Phi)_0^D$ and the other assigned to antisite defects created by atomic replacement collisions $(d\rho/d\Phi)_0^R$:

$$(d\rho/d\Phi)_0^{exp} = (d\rho/d\Phi)_0^D + (d\rho/d\Phi)_0^R. \tag{5}$$

The initial damage rate $(d\rho/d\Phi)_0^R$, due to atomic replacement collisions, was written as

$$(d\rho/d\Phi)_0^R = (d\rho/dS)_0(dS/dC_R)_0(dC_R/dC_D)_0(dC_D/d\Phi)_0 \tag{6}$$

where S is the LRO parameter; indices R, D refer respectively to replaced and displaced atoms; $d\rho/dS$ is the contribution to resistivity of a change in the long-range order parameter S; dS/dC_R refers to the variation of the LRO parameter S induced by a change of the concentration of replacements; dC_R/dC_D is the average number of replacements per displacement; and $(dC_D/d\Phi)$ is the production rate of Frenkel defects. These parameters were determined as follows:

(i) $(d\rho/dS)_0$. The electrical resistivity of long-range-ordered alloys has been theoretically calculated as a function of the degree of order (S). Rossiter (1979, 1980) improved the model of Muto and Tagaki (1955), based on the Bragg–Williams approximation, by considering that long-range atomic ordering affects the effective number of conduction electrons and by including the effect of the measurement temperature T (contribution of phonons). In a simple relaxation-time approximation, the electrical resistivity of a stoichiometric alloy is given by

$$\rho(S, T) = \rho_{dis}[(1 - S^2)/(1 - AS^2)] + (T/T_c)/(1 - AS^2) \tag{7}$$

where ρ_{dis} is the resistivity of the disordered alloy, S the Bragg–Williams LRO parameter, T_c the critical order–disorder temperature and A a parameter, the sign and amplitude of which are related to the variation of the effective number of conduction electrons with ordering. A was taken equal to zero in the theory developed by Muto and Tagaki (1955). On the other hand, Cahn *et al* (1987) considered that one of the positive values, $A = 0.75$, used by Rossiter (1980), was

consistent with the experimental data obtained by Corey and Lisowsky (1967) on the temperature dependence of the electrical resistivity of Ni_3Al alloys. Therefore, this value was used in our calculations. In the present work, the electrical resistivity was measured at 4.2 K, and then equation (7) reduces to the first term:

$$\rho(S, T) = \rho_{dis}[(1 - S^2)/(1 - AS^2)]. \tag{8}$$

For off-stoichiometric compounds, a generalized version of equation (8) was proposed by Dimitrov et al (1992b):

$$\rho(S, T) = (\rho_{dis} - \rho_{ord})[(1 - S^2/S_{max}^2)/(1 - AS^2/S_{max}^2)]. \tag{9}$$

S_{max} is the maximum value of the LRO parameter, equal to $\frac{4}{3}(1 - C_{Al})$ for $C_{Al} \geqslant 0.25$ and to $4C_{Al}$ for $C_{Al} < 0.25$; ρ_{ord} is the residual resistivity corresponding to the maximum of degree of order. Derivation of equation (9) gives for $S_0 = S_{max}$, at the beginning of irradiation:

$$(d\rho/dS)_0 = -2(\rho_{dis} - \rho_{ord})/[(1 - A)S_{max}]. \tag{10}$$

ρ_{ord} was taken equal to the residual resistivity ρ_0 measured at 4.2 K after annealing at 1173 K and slow cooling; ρ_{dis} was evaluated by extrapolation to $C_{Al} \simeq 0.25$ of the relationship given by Sitaud and Dimitrov (1990) for disordered Ni(Al) solid solutions of lower concentration:

$$\rho_{dis}(\mu\Omega\ cm) = \rho_{Ni} + (211 \pm 1)C_{Ni}C_{Al}. \tag{11}$$

(ii) $(dS/dC_R)_0$. In the stoichiometric Ni_3Al, following the consideration of the relationship between S and the number of replacement collisions in $\langle 1\,1\,0 \rangle$ rows by Becker et al (1968), we obtain (as long as $\Delta S \ll S$)

$$dS/dC_R = -(4/3)S.$$

(The coefficient 4/3 differs by a factor of 2 from the one published by Becker et al (1968); we thank Dr C Lehmann for revising the original calculations.) When $S_0 \sim 1$:

$$(dS/dC_R)_0 = -4/3.$$

(iii) $(dC_R/dC_D)_0$. The average number of replacements per displacement at the beginning of the irradiation $(dC_R/dC_D)_0$ was evaluated from the disordering rate measurements performed on single crystals of Ni_3Al in a high-voltage electron microscope (HVEM). Liu and Mitchell (1983) have shown that, at low temperature ($T \leqslant 190$ K), where vacancies are immobile, complete disordering could be achieved; this means that reordering was negligible in such irradiation conditions. From the disordering rate, a value of the number of replacements per displacement, independent of the electron flux density, was deduced. The effect of electron energy on this number was found to be small in the 0.65–1 MeV range. This agrees with the previous results of Butler and Orchard (1981), who obtained an increase of dC_R/dC_D with increasing electron energy up to 0.6 MeV and a saturation at higher energies. Both groups agree that at low temperature and high-voltage irradiation the dominant disordering mechanism was the replacement collision sequence. Consequently, we considered that the data determined in the HVEM irradiation conditions could be reasonably used in the present irradiations. The main cause of uncertainty in the determination of $(dC_R/dC_D)_0$ is the crystallographic orientation dependence, and an average value $(dC_R/dC_D)_0 = 3 \pm 1$ was introduced in the present calculations.

(iv) $(dC_D/d\Phi)_0$. This term represents the displacement cross section for Ni$_3$Al and was evaluated, with reference to pure nickel, by using the relation:

$$(dC_D/d\Phi)_0 \equiv \sigma_d^{Ni_3Al} = [(d\rho/d\Phi)_0^{Ni}/\rho_F^{Ni}](\sigma_d^{Ni_3Al}/\sigma_d^{Ni}). \qquad (12)$$

From the numerical values (table 2), it comes out that

$$\sigma_d^{Ni_3Al} = 28 \text{ barns}.$$

From the above determinations of the different factors in equation (6), we obtain the contribution of replacement sequences to the total resistivity damage rate $(d\rho/d\Phi)_0^R$, which is reported for each alloy in table 2.

Table 2. Compositions, initial resistivities ρ_0 at 4.2 K, initial damage rates $(d\rho/d\Phi)_0$ (exp = experimental, R = estimated disordering contribution, D = resulting defect contribution), relative displacement cross sections $\sigma_d^{Ni}/\sigma_d^{alloy}$ and Frenkel-pair resistivities ρ_F of the Ni$_3$Al intermetallic compounds.

Materials	Ni	Ni$_{75.4}$Al$_{24.6}$	Ni$_{75.0}$Al$_{25.0}$	Ni$_{73.5}$Al$_{26.5}$
Al (at.%)	0 (pure Ni)	24.6	25.0	26.5
$\rho_0(10^{-6}\ \Omega$ cm)	0.0430 ± 0.0002	4.90 ± 0.18	3.82 ± 0.24	14.23 ± 0.44
$(d\rho/d\Phi)_0^{exp}$ ($10^{-26}\ \Omega$ cm^3)	2.08 ± 0.04	33.9 ± 0.3	31.8 ± 0.3	29.5 ± 0.2
$(d\rho/d\Phi)_0^R$ ($10^{-26}\ \Omega$ cm^3)	—	3.1 ± 1.1	3.2 ± 1.1	2.5 ± 0.9
$(d\rho/d\Phi)_0^D$ ($10^{-26}\ \Omega$ cm^3)	2.08 ± 0.04	30.8 ± 1.4	28.6 ± 1.4	27.0 ± 1.1
$\sigma_d^{Ni}/\sigma_d^{alloy}$	1	1.103	1.105	1.112
$\rho_F(\mu\Omega$ cm/%)	6.7	109 ± 7	102 ± 7	97 ± 6

In order to obtain the initial experimental damage rate $(d\rho/d\Phi)_0^{exp}$, the resistivity damage rate data $(d\rho/d\Phi) = f(\Delta\rho_i)$ were analysed by using the same procedure and the same assumptions as those given in section 3.1 for the solid solutions. The rapid decrease of the rate observed at the beginning of the irradiation extends to a higher fluence in the stoichiometric and in the nickel-rich Ni$_3$Al compounds. Only the linear parts of the damage rate curves were fitted to equation (1) and led by extrapolation to experimental values of the initial resistivity damage rates (table 2). The comparison of these experimental damage rates with the values obtained above for the contribution of disordering shows that the latter represents only a small fraction (8–10%) of the total damage rate. Finally, the initial resistivity damage rates due to defect production $(d\rho/d\Phi)_0^D$ were obtained, according to equation (5), by subtracting $(d\rho/d\Phi)_0^R$ from the experimentally determined initial damage rates. From these data, the Frenkel-pair resistivities of the intermetallic alloys were evaluated with equation (2) by reference to the initial damage rates of pure nickel. As compared with the data relative to the pure metals, high values of the Frenkel-pair resistivity, ranging from 97 to 109 $\mu\Omega$ cm/%, were obtained (table 2); they seem to increase slightly with nickel content.

3.2.2. Discussion. In order to check the validity of the assumptions made in the preceding section for estimating the Frenkel-pair resistivities of the intermetallic compounds, we consider now two extreme assumptions concerning the relative contributions of disordering and of defect resistivity to the observed damage rates:

(i) The first one consists of assuming that defect resistivity is negligible and that all the resistivity change is due to irradiation disordering. Thus, $(d\rho/d\Phi)_0^R = (d\rho/d\Phi)_0^{exp}$. With this assumption, the average number of replacements per displacement can be evaluated in the stoichiometric alloy, by applying relationship (6). All the other factors were taken with the same values as in section 3.2.1; the calculation yields an average number of 23 replacements per Frenkel pair. This value appears very large by comparison with those, ranging between 2 and 3, obtained by Liu and Mitchell (1983) in Ni_3Al and by Becker *et al* (1968) in Ni_3Mn, for electron-irradiated samples.

(ii) The other extreme assumption consists of assigning the observed damage rate totally to defect resistivity, i.e. $(d\rho/d\Phi)_0^D = (d\rho/d\Phi)_0^{exp}$. In that case, equation (2) leads to somewhat higher values of the Frenkel-pair resistivity: 120, 113 and 106 $\mu\Omega$ cm/%, respectively for the $Ni_{75.4}Al_{24.6}$, $Ni_{75.0}Al_{25.0}$ and $Ni_{73.5}Al_{26.5}$ materials.

The relative importance of disordering produced by 3 MeV electron irradiation cannot be directly determined in the present experimental conditions. However, assuming the number of replacements per displacement to be equal to 3 ± 1, which is of the order of the values determined during electron irradiation of the $L1_2$ intermetallic compounds Ni_3Al (Liu and Mitchell 1983, Butler and Orchard 1981), Ni_3Mn (Becker *et al* 1968) and Zr_3Al (Carpenter and Schulson 1978), we find that the contribution of disordering to resistivity radiation damage represents only 8–10% of the total variation. In electron-irradiated Cu_3Au, Alamo *et al* (1983) reached similar conclusions, i.e. the contribution of disorder was smaller than 20%.

Furthermore, the following arguments show that disordering is not the main contribution to radiation damage:

(i) Studies of structural evolution of Ni_3Al compounds, during thermal treatment, have shown that the resistivity increase assigned to disordering had a larger amplitude in stoichiometric than in off-stoichiometric alloys (Sitaud *et al* 1990). Therefore, if disordering had a major contribution to radiation damage, it would be expected that the resistivity variations recorded during electron irradiation and the resistivity damage rates would be larger for the stoichiometric composition. Figures 2(a) and (b) do not show such behaviour.

(ii) In part II of the present work, devoted to damage recovery during isochronal anneals, it will be shown that the first recovery stage, the magnitude of which represents about 40% of the total resistivity recovery, does not exhibit a maximum in amplitude in the stoichiometric alloy but varies monotonically with aluminium content. Thus, at least this important part of the recovery cannot be related to some reordering process, induced by the long-range migration of point defects; it should be assigned to the annihilation of radiation-induced defects.

The Frenkel-pair resistivity values ρ_F, determined in the Ni_3Al compounds, are very large compared with those obtained in pure metals, in the present Ni solid solutions and in the $L1_2$ Cu_3Au compound (Alamo *et al* 1986). This result can be correlated to the rather large contribution of the thermal component of the resistivity (ideal resistivity, ρ_i), caused by the scattering of conduction electrons by phonons. Table 3 compares, in nickel and in the present Ni_3Al alloys, the ρ_F values and the

ideal resistivity at the Debye temperature ρ_θ^i; this parameter, which characterizes the scattering by a defined phonon population, can be considered as a measure of the scattering strength. The ρ_θ^i values were extrapolated from the ideal resistivity at 294 K by using a temperature coefficient of resistivity determined by Williams *et al* (1987), who also estimated a Debye temperature of 393 K in Ni_3Al by Callaway's (1959) formula. The general trend appears to be: the larger the ideal resistivity at the Debye temperature, the larger the Frenkel-pair resistivity. The same trend was previously observed in pure metals (Dimitrov and Dimitrov 1985) and in a series of Fe–Cr–Ni short-range-ordered alloys (Dimitrov *et al* 1990).

Table 3. Residual resistivity (at 4.2 K) $\rho_{4.2}$, ideal resistivity at 294 K ρ_{294}^i and at the Debye temperature ρ_θ^i and Frenkel-pair resistivities ρ_F in pure nickel ($\theta = 440$ K) and in the Ni_3Al compounds ($\theta = 393$ K).

Materials	Ni	$Ni_{75.4}Al_{24.6}$	$Ni_{75.0}Al_{25.0}$	$Ni_{73.5}Al_{26.5}$
$\rho_{4.2}(\mu\Omega\ cm)$	0.043	4.90	3.82	14.23
$\rho_{294}^i = \rho_{294} - \rho_{4.2}$ ($\mu\Omega\ cm$)	7.2	40.26	37.42	26.81
$\rho_\theta^i(\mu\Omega\ cm)$	8.3	47.61	44.62	32.66
$\rho_F(\mu\Omega\ cm/\%)$	6.7	109	102	97

4. Conclusions

The damage produced by 2.95 MeV electron irradiation at 4.6–9 K was investigated by electrical resistivity measurements in pure nickel, in $Ni_{94}Al_6$, $Ni_{90}Al_{10}$, $Ni_{96}Al_1Ti_3$ short-range-ordered solid solutions, and in long-range-ordered, stoichiometric and off-stoichiometric Ni_3Al compounds.

The rate of radiation damage was similar in the binary solid solutions and in pure nickel, and slightly larger in the ternary Ni(Al,Ti) alloy. Point-defect production was considered to be the main process occurring during irradiation. The analysis of damage rates leads to Frenkel-pair resistivity values close to that of pure nickel.

By contrast, in Ni_3Al compounds the resistivity damage rate was enhanced by a factor of ~ 15 with respect to pure nickel. Some contribution of disordering as a result of replacement collision sequences cannot be excluded. However, from the composition dependence of the damage rates and on account of the recovery data to be reported in part II of the present work, one has to conclude that the major part of the resistivity damage cannot be attributed to disordering. The importance of the point-defect contribution to the damage rate implies that Frenkel-pair resistivities in Ni_3Al are much larger than those usually measured in pure metals. This could be correlated with the high values of the ideal resistivity in these compounds.

References

Afyouni M, Pierron-Bohnes V and Cadeville M C 1989 *Acta Metall.* **37** 2339–47
Alamo A, De Novion C H and Desarmot G 1986 *Radiat. Eff.* **88** 69–91
Alamo A, De Novion C H, Lesueur D and Dirand M 1983 *Radiat. Eff.* **70** 157–62
Becker D, Dworschak F, Lehmann C, Rie K T, Schuster H, Wollenberger H and Wurm J 1968 *Phys. Status Solidi* **30** 219–29
Bender O and Ehrhart J 1983 *J. Phys. F: Met. Phys.* **13** 911–28
Bremer F J 1988 *Thesis* Berichte der Kernforschungsanlage Jülich, No 2199
Bremer F J, Beyss M, Karthaus E, Hellwig A, Schober T and Welter J M 1988 *J. Cryst. Growth* **87** 185–92
Butler E P and Orchard J F 1981 *Phase Stability During Irradiation* ed J R Holland, L K Mansur and D I Potter (Warrendale, PA: Metallurgical Society of AIME) pp 315–27
Cahn R W, Siemers P A, Geiger J E and Bardhan P 1987 *Acta Metall.* **11** 2737–51
Callaway J 1959 *Phys. Rev.* **113** 1046
Carpenter G J C and Schulson E M 1978 *J. Nucl. Mater.* **73** 180–9
Chassagne F, Bessière M, Calvayrac Y, Cenedese P and Lefebvre S 1989 *Acta Metall.* **37** 2329–38
Corey C L and Lisowsky B 1967 *Trans. Metall. Soc. AIME* **239** 239–43
Dimitrov C, Huguenin D, Moser P and Dimitrov O 1990 *J. Nucl. Mater.* **174** 22–34
Dimitrov C, Sitaud B, Zhang X, Dimitrov O, Dedek U and Dworschak F 1992a *J. Phys.: Condens. Matter* **4** 10211
Dimitrov C, Tarfa T and Dimitrov O 1992b *Ordering and Disordering in Alloys* ed A R Yavari (London: Elsevier Applied Science) p 130
Dimitrov O and Dimitrov C 1985 *Radiat. Eff.* **84** 117–29
Doyama M, Moser P, Huguenin D, Alamo A and Corbel C 1985 *Positron Annihilation* ed P C Jain, R M Singru and K P Gopinathan (Singapore: World Scientific) pp 903–8
Doyama M, Wang T M, Shimotomai M and Iwata T 1987 *Mater. Sci. Forum* **15–18** 1305–10
Hansen M and Anderko K 1958 *Constitution of Binary Alloys* 2nd edn (New York: McGraw-Hill)
Hilpert K, Kobertz D, Venugopal V, Miller M, Gerads H, Bremer F J and Nickel H 1987 *Z. Naturf.* **42a** 1327–33
Jung P 1981 *Phys. Rev.* B **23** 664–70
—— 1991 *Landolt-Börnstein* New Series III/25, ed H Ullmaier (Berlin: Springer) p 24
Jung P, Ansari M I, Klein H and Meertens D 1987 *J. Nucl. Mater.* **148** 148–56
Klaiber F, Schönfeld B and Kostorz G 1987 *Acta Crystallogr.* A **43** 525–33
Kozubski R and Cadeville M C 1988 *J. Phys. F: Met. Phys.* **18** 2569–75
Lifshitz I M and Slyozov V V 1961 *J. Phys. Chem. Solids* **19** 35–50
Liu H C and Mitchell T E 1983 *Acta Metall.* **31** 863–72
Muto T and Takagi Y 1955 *Solid State Physics* ed F Seitz and D Turnbull (New York: Academic) pp 193–282
Oen O S 1973 *Report* ORNL 4897
Rossiter P L 1979 *J. Phys. F: Met. Phys.* **9** 891–901
—— 1980 *J. Phys. F: Met. Phys.* **10** 1459–65
Sanchez J M, Barefoot J R, Jarrett R N and Tien J K 1984 *Acta Metall.* **32** 1519–25
Schroeder H and Schilling W 1976 *Radiat. Eff.* **30** 243–53
Shimotomai M, Wang T M and Doyama M 1983 *J. Nucl. Mater.* **116** 347–8
Sitaud B 1991 *Thesis* Université Paris VI
Sitaud B and Dimitrov O 1989 *Defect Diffus. Forum* **66–69** 477–82
—— 1990 *J. Phys.: Condens. Matter* **2** 7061–75
Sitaud B, Zhang X, Dimitrov C and Dimitrov O 1990 *Advanced Materials and Processes* vol 1, ed H E Exner and V Schumacher (Oberursell: DGM) pp 389–94
Urban R and Ehrhart P 1987 *Mater. Sci. Forum* **15–18** 1251–6
Voorhees P W 1985 *J. Stat. Phys.* **38** 231–52
Wagner C 1961 *Z. Elektrochem.* **65** 581–91
Wang T M, Shimotomai M and Doyama M 1984 *J. Phys. F: Met. Phys.* **14** 37–45
Williams R K, Graves R S and Weaver F J 1987 *J. Appl. Phys.* **61** 1486–92
Zhang X 1989 *Thesis* University of Caen