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Vacancy formation in Ni and in dilute Ni(Ge) alloys was studied under thermal equilibrium conditions using positron-annihilation Doppler broadening. A monovacancy formation enthalpy of 1.8 ± 0.1 eV was determined for pure Ni; combining this result with that from previous tracer self-diffusion measurements, a monovacancy migration enthalpy of 1.1 ± 0.1 eV was also deduced. Analysis of the vacancy-formation measurements in Ni(0.3 at.% Ge) and Ni(1 at.% Ge) yielded a value for the vacancy-Ge binding enthalpy of 0.20 ± 0.04 eV.

1. INTRODUCTION

Nickel has been widely used in recent years as a model for the study of the behavior of austenitic stainless steels under a variety of non-equilibrium atomic-defect situations caused by energetic-particle irradiation. As such, it is rather important to establish the vacancy, and other atomic-defect, properties in Ni in order to provide a firm basis for such modelling. Recent positron annihilation [1-5] and quenching [6] experiments have yielded a range of vacancy formation enthalpy values between 1.5 and 1.7 eV.

The present positron annihilation Doppler-broadening (DB) investigations of pure Ni were carried out to provide an accurate determination of the monovacancy formation enthalpy; by its comparison with the activation enthalpy for self-diffusion in the low-temperature limit, a value for the monovacancy migration enthalpy could then also be obtained. A more extensive report of some of these results has appeared elsewhere [7]. In addition, positron annihilation measurements in dilute Ni(Ge) alloys were made in order to investigate the effects of vacancy-Ge binding on vacancy formation in this system, since observations of irradiation-induced Ge segregation in Ni(Ge) as well as theoretical estimates have indicated strong vacancy-Ge binding [8].

2. EXPERIMENTAL PROCEDURE

Three samples, Ni(99.995 wt%), Ni(0.3 at.% Ge), and Ni(1 at.% Ge), were studied. The Ni(Ge) samples were produced by melting the pure Ni and Ge in an Al_2O_3 crucible, followed by an anneal for 24 h at 1390°C, in order to homogenize the alloy, in a UHV system at $p < 10^{-7}$ Torr. The spatial variation of the Ge content was subsequently analyzed in a SEM by x-ray analysis; averaging over areas of $< 10^2$ μm^2, no spatial dependence of the Ge concentration could be detected. The samples were subsequently implanted with 10^{14} atoms of ^{58}Co [9]. The Al_2O_3 crucible, which contained the sample during the DB measurements in a UHV system, was supported by a Pt/Pt-10% Rh thermocouple assembly housed in an Al_2O_3 sheath. Prior to commencing measurements, the samples were annealed in situ, the Ni for 2-3 h at ~ 1420°C and the Ni(Ge) for ~ 3 h at 1400°C. A more complete account of the experimental procedure is given elsewhere [7].

3. RESULTS AND DISCUSSION

The lineshape F(T) obtained for pure Ni is shown in Fig. 1. The result for the vacancy formation enthalpy in Ni was $H^F_{1v} = 1.76 \pm 0.12$ eV. The present work thus confirms a set of earlier measurements [7] on Ni with different Doppler-broadening equipment. A resumé of the H^F_{1v} values obtained for the four previous measurements (a,b,c,d) and the present one (e) is given in Table I. The results are consistent with a weighted average of 1.78 ± 0.07 eV; or if sample b is omitted, 1.83 ± 0.06 eV. Thus, the final value for H^F_{1v} may be conservatively taken as 1.8 ± 0.1 eV. This value may be compared to others obtained with positron annihilation: 1.5 eV [1], 1.54 eV [5], 1.55 eV [3], 1.7 eV [4],

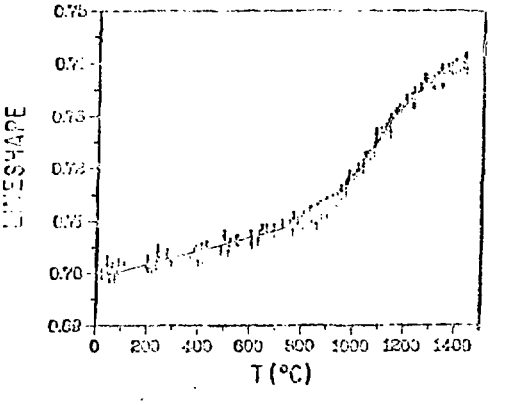

Fig. 1. Doppler-broadening lineshape versus temperature for Ni(99.995 wt.%).

Table I. Results of monovacancy formation enthalpy measurements in Ni.

Sample	# of Points	H^F_{1v} (eV)
a	82	1.79 ± 0.14
b*	96	1.58 ± 0.14
c	78	2.01 ± 0.17
d	138	1.83 ± 0.12
e	147	1.76 ± 0.12

*F(T) distinctly different from that for samples (a,c,d); see Ref. [7].

1.73 eV [2]. At present, the reason for these discrepancies is not clear, however, our experience suggests that they resulted from differing metallurgical states of the samples; a more complete discussion is found elsewhere [7]. Quenching experiments [6] yielded H^F_{1v} values of 1.58 and 1.63 eV for wire samples of 60 and 30 μm diameters, respectively. However, the observation that the larger diameter wire yielded the lower apparent formation enthalpy indicates possible vacancy loss during quenching [10]. Therefore, these values should be considered as lower limits for H^F_{1v}, consistent with the present result.

By comparing the present H^F_{1v} result to the low-temperature activation enthalpy, Q_1 = 2.88 eV, for tracer self-diffusion [11], one obtains a value for the vacancy migration enthalpy, H^M_{1v} = 1.1 ± 0.1 eV. This value is consistent with the rather limited information otherwise available for H^M_{1v} in Ni; for example, the effective migration enthalpies (1.27-0.90 eV) measured during post-quench annealing [6], the vacancy migration enthalpy of 1.2 eV estimated from direct observations of dislocation loop growth [12,13], and H_{III} ~ 1.1 eV obtained for Stage-III annealing in electron-irradiated Ni [14].

Preliminary results for Ni(1 at.% Ge) have previously been reported [15]. However, a reanalysis of these data have now lead us to conclude that the results for Ni(1 at.% Ge) previously presented were influenced by prevacancy effects [16]. In the presence of prevacancy effects, the extrapolation of the apparent bulk lineshape from low temperatures (< 600°C) leads to an underestimation of the real bulk lineshape in the knee region (~800°C) of the sigmoidal curve. If this bias is erroneously attributed to the presence of vacancy-solute pairs, as opposed to an inherent prevacancy effect (e.g., from positron trapping at impurity-pinned dislocations), then one would be led to conclude that the binding enthalpy is larger than it is in reality. Such an occurrence apparently arose in Ref. [15], where the Ni(1 at.% Ge) data were fitted to a model having a minimum number of a priori assumptions; there, the total vacancy concentration in the alloy was described as simply a superposition of two thermally-activated concentrations. In particular, both the formation entropies and enthalpies were considered as free parameters. The prevacancy effects, now known to be present in the 1% Ge alloy sample, interferred with the correct determination of the free parameters for this model. This became clear when the 0.3% Ge alloy data were analyzed in the same fashion as in Ref. [15] in combination with the previous data sets, now leading to results consistent with the Dorn-Mitchell model [17]. Since our experience with prevacancy effects for alloys is limited to our present measurements for the Ni(Ge) system, we have adopted an analysis with fewer free parameters, thereby diminishing the influence of prevacancy effects, which might still be present in our alloy samples. One might speculate that the prevacancy effects even in pure Ni have been a major contributing factor to the apparent large scatter in the results for H^F_{1v}.

The Ni(1 at.% Ge) data were analyzed simultaneously along with the present Ni(0.3 at.% Ge) data and the pure Ni data from sample e of Table I according to the model of Dorn and Mitchell [17]. Since the alloy samples are expected to contain both free and solute-bound vacancies, one needs to introduce a vacancy lineshape $F_{vi}(c,T)$ for each state, i, of vacancy present. It may also be necessary to take into account that both the magnitude and the temperature dependence of $F_{vi}(c,T)$ can depend on the solute concentration c, since the overall electronic properties are changed by the alloying. Rather than introducing this many free parameters, we used a weighted-average lineshape parameter [10], $F_v(c,T) = \Sigma\, \gamma_i(c,T) F_{vi}(c,T)$, where $\gamma_i(c,T)$ is the fraction of the trapped positrons annihilating in vacancies of type i. The temperature dependence of $F_v(c,T)$ was then approximated by $F_v(c,T) = F_v(c,0)\,[1 + \beta(c)T]$, where $F_v(c,0)$ and $\beta(c)$ were to be determined from the least-squares fitting with c = 0, 3×10^{-3}, and 1×10^{-2}. Similarly, the temperature dependence of the bulk lineshape was approximated by $F_b(c,T) = F_b(c,0)\,[1 + \alpha(c)T]$, where $F_b(c,0)$ and $\alpha(c)$ were to be determined from the fit. It should be emphasized that the introduction of an average vacancy lineshape parameter, $F_v(c,T)$, does not represent an approximation; on the other hand, the assumed linear temperature dependence of $F_v(c,T)$ does represent an approximation to its real temperature dependence.

It was further assumed that $\mu_{1v} \exp(S^F_{1v}/k) = \mu_{vs} \exp(S^F_{vs}/k)$, where μ_{1v} and μ_{vs} are the specific positron trapping rates at a free and bound vacancy, respectively, while S^F_{1v} and S^F_{vs} are the corresponding formation entropies. This approximation is expected to be valid for small vacancy-solute binding enthalpies. The analysis was carried through to first order in the solute concentration, and yielded values for the monovacancy

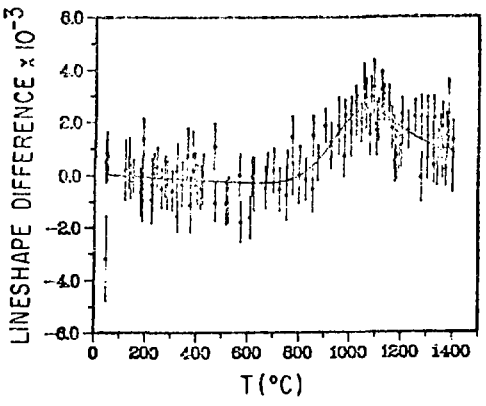

Fig. 2. Difference between Doppler-broadening curves for Ni(1 at.% Ge) and Ni(99.995 wt.%) versus temperature.

formation enthalpy, H^F_{1v} = 1.73 ± 0.08 eV, and the vacancy-Ge binding enthalpy, H^b_{vs} = 0.20 ± 0.04 eV. It is noted that this value for H^F_{1v}, obtained from the combined analysis of the three samples [Ni (Sample e of Table I), Ni(0.3 at.% Ge), Ni(1 at.% Ge)], differs slightly from the result reported for Sample e of Table I, a result of the global fit of these three samples.

The difference between the Ni(1 at.% Ge) data and the fit to the Ni(99.995 wt.%) data is shown in Fig. 2. The alloy data were shifted to coincide with those for pure Ni at 293 K. The difference between the present Fig. 2 and that found in Ref. [15] is a consequence of the more restricted Dorn-Mitchell model [17] used in the present work. The positron data are most sensitive to the presence of solute-bound vacancies in an intermediate temperature region (~1355 K for 1 at.% Ge). At this temperature, the single-solute-bound vacancies account for ~40% of all vacancies in the Ni(1 at.% Ge) sample. One might thus expect that some manifestation of higher-order, vacancy-solute clusters should be present in the data. Evaluation of the second-order term in the Dorn-Mitchell expression [17], however, indicates that for the Ni(1 at.% Ge) sample at 1355 K, vacancies bound to two solute atoms (Ge dimers) would account for only 0.4%, 2.2% or 11% of the vacancies in the system, for vacancy-Ge dimer binding enthalpies of 0, 0.2, or 0.4 eV, respectively. Thus, unless the binding enthalpy for such a cluster were large (> 0.4 eV), it would be unlikely that higher-order clusters could be detected in the present experimental data. An analysis of the present data including a second-order term in the solute concentration confirmed that no clusters could be detected, indicating binding enthalpies of vacancy-Ge dimer clusters $\lesssim$ 0.4 eV. Further support for this was established by analyzing the Ni and Ni(0.3 at.% Ge) data alone, omitting the Ni(1 at.% Ge) data; the result was H^b_{vs} = 0.25 ± 0.09 eV, in reasonable agreement with the result obtained from the combined analysis, 0.20 ± 0.04 eV.

In conclusion, the present work has shown that the monovacancy formation enthalpy in Ni is 1.8 ± 0.1 eV and that, when this is compared to the low-temperature activation enthalpy for self-diffusion, a monovacancy migration enthalpy of 1.1 ± 0.1 eV is obtained. An analysis of the Ni(Ge) alloy data has yielded a value for the vacancy-Ge binding enthalpy of 0.20 ± 0.04 eV, which is considerably smaller than a previous theoretical estimate [8] would have suggested.

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