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Site-distributions of Fe alloying additions to B2-ordered NiAl☆

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Abstract

The site-distributions of Fe alloying additions to B2-ordered NiAl alloys have been measured by ALCHEMI (atom location by channeling-enhanced microanalysis). Twelve alloy compositions were examined, of stoichiometries $Ni_{50-x}Al_{50}Fe_x$ (Ni-deficient), $Ni_{50}Al_{50-x}Fe_x$ (Al-deficient), and $Ni_{50-x/2}Al_{50-x/2}Fe_x$ (intermediate), with four different alloying levels, $x = 0.25$, 2, 5, and 10. The data indicate that Fe tends to act as a buffer between the two sublattices, preferentially occupying the site of the stoichiometrically deficient host element. However, the Fe alloying addition was found to partition between the two sublattices to some extent in all alloys, so that 'Ni'-site vacancies or Ni anti-site defects are required to maintain the site balance. The observed trends in the site-distributions suggest that the range of compositions reported by Darolia et al. (Darolia R, Lahrman DF, Field RD. Scripta Metall Mater 1992;26:1007). to exhibit enhanced ductility may coincide with an inversion in the site-substitution behavior, where more Ni than Fe occupies the aluminum sublattice. Published by Elsevier Science Ltd.

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1. Introduction

The B2-ordered intermetallic alloy NiAl is an attractive candidate material to replace Ni-base superalloys for high-temperature applications in the next generation of gas turbine engines because of its combination of high melting temperature, good oxidation resistance, high thermal conductivity and low density. However, the usefulness of NiAl as a high-temperature material is limited at present by its low strength in the unalloyed condition and by its low fracture toughness and plasticity at ambient temperatures. Minor alloying additions to NiAl have been shown to improve either the high-temperature strength [1,2] or ambient-temperature ductility [3] of these alloys. However, while extensive research has been devoted to alloy development in NiAl, the influence of alloying additions on the mechanical properties of NiAl is at present poorly understood, and cannot be fully explained with models that work for alloying effects in simple metals [4].

Among the many elements that have been studied as possible microalloying additions to NiAl, Fe has been of particular interest. The substitution of Fe for Ni in NiAl has been shown to increase the flow stress of the alloy during creep tests, with the maximum effect observed at around 10 at% Fe [5]. The effect of small amounts of Fe on the ductility of NiAl has been of even greater interest. The addition of 0.1–0.25 at% Fe to NiAl has been shown to result in up to a six-fold increase in the ambient-temperature ductility of single crystals oriented along "soft" directions [3]. However, subsequent studies have shown that these improvements in ductility do not extend to polycrystalline specimens [6,7]. It is currently hypothesized that the increase in ductility results from the interaction of the alloying element with interstitial impurities [8], such as C [9]. The strong strain aging effect in NiAl [10] and the strong dependence of ductility on crystal purity [11] are consistent with this hypothesis. The imperfect understanding of the ductilization effect of Fe in NiAl has not

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prevented its exploration for technological applications. Recently published studies on the development of NiAl microalloyed with Fe focus on single-crystal growth [12] and on metal-matrix composites of NiAl(Fe) and Al_2O_3 [13]. However, an improved fundamental understanding of the nature of the Fe-enhanced ductility of NiAl single crystals would further the ability of materials development engineers to capitalize on the beneficial effects of microalloying NiAl with Fe.

The purpose of the present study is to measure the site-substitution behavior of Fe in B2-ordered nickel aluminides for four alloying levels up to 10 at% Fe in Ni-deficient (50 at% Al), Al-deficient (50 at% Ni) and intermediate (equal at% of Ni and Al) series of alloys. The site distributions of Fe have been measured by ALCHEMI (atom location by channeling-enhanced microanalysis) [14]. Early formulations [15] of ALCHEMI gave gross systematic errors in the site-distributions of aluminide intermetallics [16,17], because of the effects of ionization delocalization, which can be pronounced for soft Al K X rays. However, recent improvements in the technique with respect to statistical confidence [18,19], ionization delocalization [20,21], and anti-site defects [21,22], have made ALCHEMI a reliable technique for the analysis of site-distributions in ordered aluminides. However, recent formulations that do not include the effects of ionization delocalization are not expected to yield accurate site distributions [23,24]. With explicit correction for the effects of ionization delocalization, ALCHEMI now yields site distributions that are sufficiently reliable that other alloy properties can be understood on the basis of these measurements. For example, a recent systematic study of 3d transition elements in B2-ordered iron aluminides has been used to show the relative influences of alloy thermodynamics and kinetics in alloy processing [25]. The present paper is part of a more comprehensive study aimed at correlating the site substitution behavior of Fe in NiAl with the mechanical properties of the alloys [26]. These data have been published in a preliminary form elsewhere [27].

2. Experimental procedure

Twelve different alloys were prepared for this study, with stoichiometries $Ni_{50-x}Al_{50}Fe_x$ (Ni-deficient), $Ni_{50-x/2}Al_{50-x/2}Fe_x$ (intermediate), and $Ni_{50}Al_{50-x}Fe_x$ (Al-deficient), and with $x = 0.25$, 2, 5, and 10. Care was taken to ensure that the processing and analysis of the twelve alloys were performed in a similar fashion. The starting materials used to make the alloys were of high purity: 99.95%-pure Ni, 99.99%-pure Al and 99.99%-pure Fe. Alloys containing 0.25 at% Fe were made from a master ingot, which had a composition determined by physical property measurements to be very close to stoichiometric NiAl. These alloys were made by adding carefully weighed amounts of Fe and an equal mol fraction of Al, Ni + Al, or Ni to specimens cut from the master ingot. All alloys were arc-melted and drop-cast into water-chilled Cu molds. The weight loss for most alloys was determined to be $< 0.3\%$. All alloys were homogenized under vacuum at 1300°C for 5 h, then step-cooled to room temperature with the following cycle: 1100°C for 24 h, 900°C for 48 h, and 800°C for 168 h. The alloys were then annealed under vacuum at 800°C for 72 h and water quenched. Three-millimeter discs were spark-cut from 150- to 250–μm-thick slices of each alloy and thinned with a Tenupol twin-jet polishing system in a solution of 6% perchloric acid, 34% *N*-butyl alcohol, and 60% methanol at a temperature of −20°C and with an electric current of 110 mA.

Energy-dispersive X-ray (EDX) spectra were acquired with a Philips CM12 operated at 120 kV and equipped with a LaB_6 filament, an EDAX 9900 spectrometer and superUTW Si(Li) detector. For all acquisitions, the specimen was cooled to −130°C (143 K) to inhibit contamination buildup and to reduce thermal vibrations of the atoms about their crystallographic lattice sites, which mitigate the channeling effects. In addition, the self-supporting disc specimens were masked with a gold washer with a 600-μm-diameter aperture in order to reduce secondary excitation effects, especially secondary fluorescence of Fe-K X rays by Ni-K X rays excited in the analyzed region of the specimen [28,29]. Experiments were performed with an incident beam divergence semi-angle of 3 mrad, which is approximately one-half the Bragg angle for 100 reflections, the lowest-order reflections excited. (Adequate site discrimination is obtained as long as the beam-divergence semi-angle is small in comparison with the Bragg angle of the relevant superlattice reflection.) For all specimens, spectra were acquired at an identical series of orientations near [014] beam direction at 10 distinct excitations of the h00 systematic row of reflections between the symmetry (with h00 and −h00 reflections equally excited) and the 600 Bragg conditions. Diffracting conditions were chosen with great care to minimize the excitation of non-systematic reflections, which could potentially complicate the interpretation of the channeling data. In addition, the electron beam tilt controls were used to vary the orientation of the beam relative to the specimen in order to ensure that the absorption correction for the Al-K X rays would be identical for the entire series of spectra. The probe current was monitored and held at a constant value throughout the acquisition of the series of spectra. The intensities of the K_α lines of all elements were measured for ALCHEMI analysis. In order that there would be a similar statistical significance for each data point, all spectra were acquired so as to obtain a similar number of counts in the K_α peak of the Fe alloying element. Two independent analyses were performed on each of the alloys with 0.25

at% Fe, given the relatively poor statistical confidence of these measurements. An additional analysis was also performed on the alloy of composition $Ni_{50}Al_{48}Fe_2$.

Extraction of the parameters of interest from the raw data was performed with software developed at Oak Ridge National Laboratory. The theory of the ALCHEMI formulation used for the data analysis has been outlined elsewhere [21,25]. For the data reduction, the statistical significance for each measured characteristic intensity is weighted according to $1/\sqrt{N}$ Poisson statistics. Coefficients α_{FeNi} and α_{FeAl} were extracted by linear regression analysis of $(r_{Fe}-1)$ with respect to $(r_{Ni}-1)$ and $(r_{Al}-1)$, where $r_X = I_X/I_X^{(0)}$ is the measured intensity I_X of the characteristic X-ray line of element X divided by the corresponding intensity $I_X^{(0)}$ acquired at a reference orientation at which electron channeling is negligible. The normalized data form a plane in the three-dimensional space defined by (r_{Ni}, r_{Al}, r_{Fe}) and the linear regression coefficients α_{FeX} can be visualized geometrically as the planar coefficients of the data. Correlation coefficients χ_{FeNi}, which are corrected for the effects of ionization delocalization, were extracted from α_{FeNi} and α_{FeAl} with a single delocalization correction factor $L_{NiAl} = 1.379 \pm 0.009$ for all alloys, which was measured from the $Ni_{50}Al_{40}Fe_{10}$ alloy at several orientations along the 110 Kikuchi band. For {110}, the channeling effect is pronounced but there is no discrimination between the 'Ni' and 'Al' sublattices [25,30]. This delocalization-corrected coefficient χ_{FeNi} is a first-order approximation to the actual site-occupancy $p_{Fe'Ni'}$,[2] and is equal to the site occupancy as long as there are no anti-site defects. The calculation of $p_{Fe'Ni'}$ from χ_{FeNi} when there are anti-site defects has been discussed elsewhere [25].

3. Results

Measured linear regression coefficients α_{FeNi} and α_{FeAl}, and calculated correlation coefficients χ_{FeNi}, delocalization correction coefficients L_{NiFe}, and site-distributions $p^0{}_{Fe'Ni'}$ are summarized in Table 1. Point-defect concentrations consistent with $p^0{}_{Fe'Ni'}$ and the nominal alloy compositions are shown in Table 2, along with the corresponding compositions of the 'Ni' and 'Al' sublattices. It is assumed that the point defects necessary to maintain the site balance are vacancies on the 'Ni' sublattice for the Ni-deficient alloys and Ni anti-site atoms on the 'Al' sublattice for the intermediate and Al-deficient alloys [31]. The coefficients L_{NiFe} are a measure of the relative delocalization of the Fe and Ni K X-rays, and are expected to be unity [25,30]. In accordance with this expectation, the weighted average of the coefficients in Table 1 is $\langle L_{NiFe} \rangle = 0.996 \pm 0.005$. For individual measurements, the condition $L_{NiFe} = 1$ means that the parameters α_{FeNi} and χ_{FeNi} are equal, and there is satisfactory agreement between these parameters for most measurements. The exception to this general agreement is the Ni-deficient alloy with the dilute Fe alloying level, $x = 0.25$. For both measurements from this alloy, the coefficient α_{FeNi} is smaller than χ_{FeNi}. These differences indicate that not all of the Fe in the analyzed region of the specimen correlates with the host elements, and may arise, for example, from an Fe-enriched oxide scale. The superscripted "0" on the site-distribution $p^0{}_{Fe'Ni'}$ denotes that the site distribution was calculated under the assumption that the alloy contains the minimum point-defect populations consistent with the measured χ_{FeNi}. ALCHEMI does not provide an independent measure of vacancy and anti-site defect concentrations and hence the value of $p_{Fe'Ni'}$ must be calculated assuming likely concentrations for these defects. The values $p^0{}_{Fe'Ni'}$ are calculated assuming that the alloys contain only one type of defect (vacancy or anti-site) and that the defect concentration is the minimum consistent with χ_{FeNi}. Generally, if there are additional (e.g. thermal) defects, the correction to $p_{Fe'Ni'}$ is small. For example, a vacancy concentration of 3.8% would be required in order for the correction to the site distribution of the $Ni_{50}Al_{40}Fe_{10}$ alloy to be equal in size to its statistical error. However, the superscripted "0" serves as a reminder that the calculated $p_{Fe'Ni'}$ is not unique.

The site distributions $p^0{}_{Fe'Ni'}$ are plotted in Fig. 1 as a function of the atomic percentage of the Fe alloying element. For alloys where two independent analyses were performed, the weighted average of the measurements is plotted. It is noteworthy that the Fe alloying element partitions between the two sublattices to some extent in all the alloys, so that 'Ni'-site vacancies or Ni anti-site atoms on the 'Al' sublattice are required to maintain the site balance. In the Ni-deficient series of alloys, the Fe predominantly occupies the 'Ni' sublattice, with ~90% 'Ni'-site occupancy at low alloying levels ($x = 0.25$, 2) and ~95% 'Ni'-site occupancy at the higher alloying levels ($x = 5$, 10). For the alloys in the intermediate series, slightly more than half of the Fe is found on the 'Ni' sublattice at all alloying levels, with a slight downward trend in the 'Ni' site occupancy with Fe concentration, from ~63% ($x = 0.25$) to ~57% ($x = 10$). A more pronounced downward trend in the 'Ni' site occupancy is observed in the Al-deficient series, from ~31% ($x = 2$) to ~24% ($x = 10$). However, in the Al-deficient alloy with $x = 0.25$, the 'Ni' site occupancy is steeply higher, with a partitioning similar to the corresponding alloy of intermediate stoichiometry. The poor agreement between the two measurements in this alloy, which contrasts with the excellent agreement for

[2] The notation is designed to distinguish between a host element (e.g. Ni) and the regular lattice site occupied by the host element in the defect-free stoichiometric crystal (e.g. 'Ni').

Table 1
Parameters measured and calculated from ALCHEMI analysis (see text for details)

Alloy series	x	α_{FeNi}	α_{FeAl}	χ_{FeNi}	L_{NiFe}	$p^0_{Fe'Ni'}$ (%)
$Ni_{50-x}Al_{50}Fe_x$ (Ni-deficient)	0.25	0.788 ± 0.075	0.129 ± 0.110	0.894 ± 0.081	1.135 ± 0.142	89.4 ± 8.1
		0.673 ± 0.061	0.085 ± 0.096	0.916 ± 0.087	1.362 ± 0.173	91.6 ± 8.7
	2	0.955 ± 0.028	0.172 ± 0.049	0.884 ± 0.029	0.926 ± 0.040	88.4 ± 2.9
	5	0.965 ± 0.009	0.049 ± 0.012	0.964 ± 0.009	1.000 ± 0.013	96.4 ± 0.9
	10	0.951 ± 0.007	0.064 ± 0.010	0.953 ± 0.007	1.003 ± 0.010	95.3 ± 0.7
$Ni_{50-x/2}Al_{50-x/2}Fe_x$ (intermediate)	0.25	0.565 ± 0.063	0.464 ± 0.108	0.627 ± 0.060	1.109 ± 0.125	62.6 ± 6.0
		0.673 ± 0.039	0.543 ± 0.072	0.631 ± 0.034	0.937 ± 0.059	63.1 ± 3.4
	2	0.605 ± 0.032	0.589 ± 0.059	0.587 ± 0.027	0.969 ± 0.051	58.5 ± 2.7
	5	0.559 ± 0.016	0.554 ± 0.017	0.582 ± 0.010	1.040 ± 0.023	57.7 ± 1.0
	10	0.578 ± 0.020	0.586 ± 0.029	0.576 ± 0.015	0.997 ± 0.029	56.8 ± 1.3
$Ni_{50}Al_{50-x}Fe_x$ (Al-deficient)	0.25	0.541 ± 0.060	0.760 ± 0.085	0.495 ± 0.039	0.916 ± 0.075	49.4 ± 3.9
		0.588 ± 0.024	0.511 ± 0.041	0.613 ± 0.021	1.044 ± 0.042	61.1 ± 2.1
	2	0.291 ± 0.021	0.964 ± 0.037	0.294 ± 0.017	1.011 ± 0.035	29.0 ± 1.6
		0.345 ± 0.029	0.926 ± 0.038	0.340 ± 0.021	0.984 ± 0.040	33.5 ± 2.0
	5	0.279 ± 0.025	0.992 ± 0.034	0.280 ± 0.019	1.002 ± 0.036	27.2 ± 1.8
	10	0.263 ± 0.013	1.100 ± 0.024	0.248 ± 0.010	0.943 ± 0.020	23.7 ± 0.9

Table 2
Calculated point defect concentrations and sublattice compositions

Alloy series	x	$\mathbf{V}^0$ (%)[a]	$\mathbf{p}^0_{Ni'Al'}$ (%)	'Ni'-site composition	'Al'-site composition
$Ni_{50-x}Al_{50}Fe_x$ (Ni-deficient)	0.25	0.05 ± 0.04		$[Ni_{49.75}Fe_{0.22}\mathbf{V}^0_{0.05}]$	$[Al_{50}Fe_{0.03}]$
		0.04 ± 0.04		$[Ni_{49.75}Fe_{0.23}\mathbf{V}^0_{0.04}]$	$[Al_{50}Fe_{0.02}]$
	2	0.46 ± 0.12		$[Ni_{48}Fe_{1.77}\mathbf{V}^0_{0.46}]$	$[Al_{50}Fe_{0.23}]$
	5	0.35 ± 0.09		$[Ni_{45}Fe_{4.82}\mathbf{V}^0_{0.35}]$	$[Al_{50}Fe_{0.18}]$
	10	0.92 ± 0.14		$[Ni_{40}Fe_{9.53}\mathbf{V}^0_{0.92}]$	$[Al_{50}Fe_{0.47}]$
$Ni_{50-x/2}Al_{50-x/2}Fe_x$ (intermediate)	0.25		0.06 ± 0.03	$[Ni_{49.84}Fe_{0.16}]$	$[Al_{49.88}Fe_{0.09}Ni_{0.03}]$
			0.07 ± 0.02	$[Ni_{49.84}Fe_{0.16}]$	$[Al_{49.88}Fe_{0.09}Ni_{0.03}]$
	2		0.34 ± 0.11	$[Ni_{48.83}Fe_{1.17}]$	$[Al_{49}Fe_{0.83}Ni_{0.17}]$
	5		0.81 ± 0.10	$[Ni_{47.11}Fe_{2.89}]$	$[Al_{47.5}Fe_{2.11}Ni_{0.39}]$
	10		1.50 ± 0.28	$[Ni_{44.32}Fe_{5.68}]$	$[Al_{45}Fe_{4.32}Ni_{0.68}]$
$Ni_{50}Al_{50-x}Fe_x$ (Al-deficient)	0.25		0.25 ± 0.02	$[Ni_{49.88}Fe_{0.12}]$	$[Al_{49.75}Fe_{0.13}Ni_{0.12}]$
			0.31 ± 0.01	$[Ni_{49.85}Fe_{0.15}]$	$[Al_{49.75}Fe_{0.10}Ni_{0.15}]$
	2		1.16 ± 0.07	$[Ni_{49.42}Fe_{0.58}]$	$[Al_{48}Fe_{1.42}Ni_{0.58}]$
			1.34 ± 0.08	$[Ni_{49.33}Fe_{0.67}]$	$[Al_{48}Fe_{1.33}Ni_{0.67}]$
	5		2.72 ± 0.18	$[Ni_{48.64}Fe_{1.36}]$	$[Al_{45}Fe_{3.64}Ni_{1.36}]$
	10		4.73 ± 0.19	$[Ni_{47.63}Fe_{2.37}]$	$[Al_{40}Fe_{7.63}Ni_{2.37}]$

[a] Vacancy concentration $\mathbf{V}^0$ represents the percentage of all regular lattice sites.

the corresponding Ni-deficient and intermediate alloys, may indicate that the site occupancy is strongly influenced by local compositional fluctuations. However, the measurements indicate that half or more of the Fe alloying element occupies the 'Ni' sublattice in these Al-deficient alloys.

4. Discussion

4.1. Effect of secondary fluorescence on ALCHEMI measurements

Secondary fluorescence is a potential source of systematic error for these ALCHEMI measurements [28]. This artifact—the fluorescence of characteristic X rays far from the analyzed volume of the specimen by primary X rays of higher energy—is most pronounced when the energy of the primary X-ray is just above the ionization threshold of the fluoresced element, as is the case for the fluorescence of Fe by Ni. This extraneous fluoresced Fe intensity is produced by Ni X rays excited in the analyzed volume of the specimen and therefore it mimics the variation of the Ni X-ray intensity. Since site distributions are determined with ALCHEMI by correlating the variation of the X-ray intensity of the Fe alloying element with those of the Ni and Al host elements, the fluoresced Fe intensity may be misinterpreted as Fe partially occupying the 'Ni' sublattice. In the present study, the fluorescence has been greatly reduced by

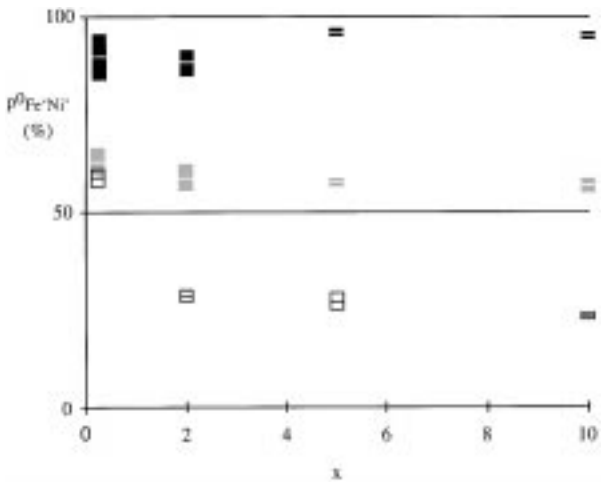

Fig. 1. Percentage of Fe occupying the 'Ni' sublattice ($p^0_{Fe'Ni'}$) as a function of the atomic percentage x of the Fe alloying element, for alloys of stoichiometry $Ni_{50-x}Al_{50}Fe_x$ (black), $Ni_{50}Al_{50-x}Fe_x$ (white), and $Ni_{50-x/2}Al_{50-x/2}Fe_x$ (grey). The vertical spread for each data point represents ± one standard deviation.

masking the majority of the self-supporting disc with an X-ray opaque gold washer. Although it is difficult to calculate the fluorescence from the irregularly shaped electropolished specimen, the fluorescence can be approximated as that of a dimpled and ion-milled specimen, which has a similar geometry [29]. To a good approximation, the intensity of Fe-K X rays fluoresced by Ni-K X rays is proportional to both the Fe concentration (x), and the fraction of the Fe on the 'Al' sublattice ($1-p^0_{Fe'Ni'}$). The correction is therefore largest for the alloy of composition $Ni_{50}Al_{40}Fe_{10}$. Even for this specimen, we calculate that the systematic shift in the site-occupancy is at most 0.6%, which is smaller than the statistical error for $p^0_{Fe'Ni'}$. The systematic error for the Ni-deficient alloys ($p^0_{Fe'Ni'}\approx 1$) or the dilute alloys ($x=0.25$) is negligible. Even if the contribution of the fluorescence has been underestimated, the effect of the fluorescence would be to predict that the alloys have a greater 'Ni' sublattice occupancy as the concentration of the Fe increased, which is opposite to the trend observed in the alloys of Al-deficient and intermediate stoichiometry. These trends could not therefore be primarily due to fluorescence.

4.2. Comparison with previous studies

These ALCHEMI results contradict the results of atom probe field ion microscopy (APFIM) performed in the context of this study [32]. The atom probe measurements indicated that Fe principally occupies the 'Al'-site in both Ni-deficient and Al-deficient NiAl. However, these APFIM results were contradicted by subsequent ALCHEMI [33] and X-ray diffraction [34] measurements, and it is currently believed that the APFIM measurements of site-distributions in these alloys give a misleading result due to preferential evaporation rates of the elements composing the alloy [26].

The results of the present study are in good general agreement with the extended X-ray absorption fine-structure (EXAFS) analysis of Chartier et al. [35]. These authors compare the EXAFS oscillations of Fe in two ternary alloys with those of Ni in binary stoichiometric NiAl. Similarity in such oscillations suggests a similar local chemical environment and provides a qualitative measure of the site occupation of the alloying element. Their data show that a strong similarity exists between the oscillations of the two transition elements in an alloy of composition $Ni_{46}Al_{52}Fe_2$, but not in an alloy of composition $Ni_{50}Al_{49}Fe_1$. The results of the present study indicate that Fe should occupy the 'Ni' sublattice almost exclusively in the first alloy, so that Fe and Ni would indeed have similar local chemical environments, whereas Fe should either partition evenly or mostly occupy the 'Al' sublattice in the second alloy, so the EXAFS oscillations would be substantially different. However, our measurements do not substantiate the authors' claim that Fe occupies the 'Al' sublattice exclusively in Al-deficient $Ni_{50}Al_{50-x}Fe_x$.

These measurements agree qualitatively with the calculations of Kao et al. [36], which are based upon a simple thermodynamic model. These authors predict a site preference for the 'Al' sublattice for Fe relative to the Ni host element. In accordance with these predictions, all of the measurements in the present paper show a greater 'Al' sublattice occupancy for the Fe alloying element than would occur if Ni and Fe were chemically identical. For example, in the $Ni_{50}Al_{40}Fe_{10}$ alloy, our measurements indicate that ~24% of the Fe occupies the Ni sublattice, which is much smaller than the ~83% that would be consistent with chemical similarity between Ni and Fe. These authors also compare model predictions with a preliminary ALCHEMI study of similar alloys by the present authors [33] which showed substantially similar results for the $Ni_{50}Al_{40}Fe_{10}$ and $Ni_{40}Al_{50}Fe_{10}$ alloys, and state that their model predictions are in good qualitative agreement with these ALCHEMI measurements.

The site distributions determined by ALCHEMI in this study are in excellent agreement with the magnetic susceptibility and nuclear magnetic resonance (NMR) measurements of Golberg and Shevakin [37]. These authors examine a variety of alloy compositions, including several alloys in the families of Ni-deficient, Al-deficient, and intermediate compositions examined in the present study. The detection of local magnetic moments (LMMs) in all alloys of these compositions was taken as evidence that at least some of the Fe alloying element occupies the 'Al' sublattice, in agreement with our measurements. Among the Fe-containing alloys examined by the authors, only those with an Al excess, of stoichiometry $Ni_{46-x}Al_{54}Fe_x$, exhibited the

Pauli (temperature-independent) paramagnetism of the binary alloys, consistent with Fe occupying only the 'Ni' site in these Al-rich alloys. The excellent agreement between our spectroscopic measurements of the site occupancies and these magnetic susceptibility measurements support the theoretical prediction based on first-principles calculations that magnetic susceptibility should be an excellent indicator of sublattice occupancies of Fe in NiAl [38]. The NMR measurements of Golberg and Shevakin [37] are interpreted as resulting from changes in the chemical environment (occupancy of first and to some extent second atomic coordination shells) of the Al host atoms. From the NMR measurement of Ni-deficient alloys similar to those examined in the present study, the authors were able to estimate that 7–11% of the Fe occupies the 'Al' sublattice, in excellent agreement with our spectroscopic measurements. The authors' suggestion, based on the large LMMs measured in alloys of intermediate compositions, that Fe has an 'Al' site preference, is not in agreement with our measurements. The exceptionally large LMMs measured by the authors are more consistent with the hypothesis that a significant amount of Fe on both sublattices gives rise to a cooperative effect, so that the LMMs in these alloys cannot be interpreted in terms of a simple linear correlation with 'Al' site occupancy.

The results of the present study agree in many important respects with trends in the site occupations for Fe in NiAl that were predicted by Fu and Zou on the basis of first-principles calculations [38]. These authors calculate that Fe has a strong preference (2.5 eV) for the 'Ni' sublattice for alloys with $\geqslant 50$ at% Al but a weak preference (0.1 eV) for the 'Al' sublattice in alloys with $\geqslant 50$ at% Ni. Consequently, the authors argue that Fe should exclusively occupy the 'Ni' sublattice in the Ni-deficient alloys of the present study, since the large enthalpy term dominates, whereas Fe should partition between the two sublattices in the Al-deficient and intermediate alloys, with an increasing 'Al' sublattice occupancy at higher Fe concentrations (x), since these site occupancies should be strongly influenced by configurational entropy. In accordance with these predictions, our measured site-occupancies show that Fe predominantly occupies the 'Ni' sublattice in the Ni-deficient alloys and shows an increasing 'Al' sublattice occupancy with increasing Fe concentration in the Al-deficient and intermediate alloys. Our results also show a pronounced increase in 'Ni' sublattice occupancy for $x = 0.25$ relative to $x = 2$ for the Al-deficient alloys and also to a lesser extent for the intermediate alloys. These trends are also qualitatively consistent with the theoretical prediction of Fu and Zou [38] that Fe should have a 'Ni' sublattice preference for all three alloy series at low Fe concentrations. The slight absolute 'Ni' sublattice preference for Fe in the alloys of intermediate stoichiometry is also consistent with these authors' calculated site preference energies, since an absolute 'Al' sublattice preference would require the production of 'Ni'-site vacancies, with an energy cost of about 1.3 eV per Fe atom. Some quantitative discrepancies remain between our measurements and the theoretical predictions of Fu and Zou [38]. A small fraction (4–11%) of the Fe is found to occupy the 'Al' sublattice at all alloying levels in the Ni-deficient alloys, whereas the calculated 2.5 eV site-preference energy suggests that Fe should occupy the 'Ni' sublattice exclusively. Also, the theoretical predictions of Fu and Zou [38] indicate a much stronger dependence on Fe concentration for the site-occupancies of Fe in the Al-deficient alloy, and a smaller 'Al' sublattice occupancy, than is observed experimentally. Our results would seem to indicate a larger preference for the 'Al' sublattice for Fe in Al-deficient alloys than the 0.1 eV calculated by Fu and Zou [38].

There is better quantitative agreement between our experimental results and the results of tight-binding calculations performed by Shinoda et al. [39]. These authors plot the site-occupancies and point-defect concentrations at 1000°C for alloys with aluminum concentrations between 38 and 50% and with a Ni:Fe concentration ratio of 9:1. The results for the three alloys with $x = 5$ of the present study can be compared with alloys of composition $Ni_{45}Al_{50}Fe_5$, $Ni_{47.4}Al_{47.4}Fe_{5.3}$, and $Ni_{50}Al_{44.4}Fe_{5.6}$ in the paper of Shinoda et al. [39]. The fraction of Fe on the 'Ni' sublattice calculated for these three alloys are approximately 97, 55 and 18%, which compare well with our experimental values of 96.4 ± 0.9, 57.7 ± 1.0 and 27.2 ± 1.8%. Although a direct comparison of values would be suspect given the difference in equilibration temperature, these values are in better quantitative agreement with our results than the calculated values of Fu and Zou [38]. In particular, the prediction of Shinoda et al. [39] that a small fraction of the Fe occupies the 'Al' sublattice in the Ni-deficient alloy is consistent with our measurements.

Finally, our results are in good agreement with vacancy and hardness measurements performed on similar alloys by Pike et al. [40]. These authors show that the vacancy concentration in the Ni-deficient series of alloys increases with increasing Fe concentration, with a corresponding increase in hardness. This result is consistent with the residual 'Al'-site occupancies of Fe alloying additions to the Ni-deficient alloys in the present study, since any Fe on the Al sublattice must be compensated by a proportionate concentration of 'Ni'-site vacancies in order to maintain the site balance. Since vacancies are such a potent strengthening mechanism in these B2-ordered alloys, the hardness measurements are a sensitive indicator of the atomic site distributions and, like the magnetic susceptibility measurements [37], substantiate the small residual concentrations of Fe on the 'Al' sublattice measured by ALCHEMI in the Ni-defi-

cient alloys. Pike et al. [40] also perform hardness measurements on alloys in the series $Ni_{60-x}Al_{40}Fe_x$, and report alloy softening with increasing Fe concentration up to $x=10$. The mechanism proposed by the authors, that the softening results from the displacement of Ni by Fe on the 'Al' sublattice—Ni anti-site defects being a more potent hardener than $Fe_{\cdot Al'}$ substitutional defects—is also consistent with the substitution of Fe on the 'Al' sublattice in our series of Al-deficient alloys. More generally, the link among the site distribution of the alloying element, the resulting vacancy or anti-site defect concentrations and the hardness suggests the possibility that the mechanical properties of intermetallic alloys might be engineered if the site substitution behavior of the alloying element is sufficiently understood.

4.3. Correlation of site-occupancies with ductility measurements

Darolia et al. [3] have reported that there is a significant ductility enhancement in NiAl single crystals if Fe is substituted for Al with alloying concentrations between 0.1 and 0.25 at%. It is noteworthy that among the 12 alloy compositions of the present study, only the alloy composition corresponding to this region of enhanced ductility exhibits a substantial change in the site-substitution behavior of the Fe alloying element. As shown in Fig. 1, there is a sharp discontinuity in the Al-deficient series of alloys in the site distribution of the Fe at the 0.25% alloying level relative to the 2, 5 and 10% alloying levels, in contrast with little or no variation in the site distribution observed in the Ni-deficient and intermediate alloy series. From Table 2, the distinguishing characteristic of this alloy relative to all others in this study is that the amount of Ni is beginning to exceed the amount of Fe on the 'Al' sublattice. If the trend in the data were to extend to Fe concentrations less than 0.25%, as predicted by Fu and Zou [38] on the basis of configurational entropy, then the range of alloy compositions reportedly exhibiting enhanced ductility would correspond to alloys exhibiting an "inversion" of the 'Al' sublattice concentrations of Ni and Fe. Note that the discrepancy in the two measurements from this alloy, suggesting a strong dependence on local compositional fluctuations, is consistent with a rapid variation in site-occupancy with composition, so that it is possible that at the 0.1 at% alloying level, nearly all of the Fe may occupy the 'Ni' sublattice, requiring an equal concentration of Ni anti-site defects.

It remains to identify a mechanism by which such an inversion in the site substitution behavior might effect the observed ductility enhancement. Such a mechanism would need to depend principally on the point-defect structure of the alloy, namely on $Fe_{\cdot Ni'}$ substitutional defects and $Ni_{\cdot Al'}$ anti-site defects, rather than on extended defects such as dislocations. A possible mechanism that is consistent with current hypothesis regarding the effect of interstitial defects [8–11] is the elastic interaction between these interstitial defects and the substitutional point defects. The size of the Fe alloying element is intermediate between those of the host elements. In close proximity to one another, $Fe_{\cdot Ni'}$ and $Ni_{\cdot Al'}$ would be expected to form a stress dipole, which could potentially act as a getter for interstitial impurities and mitigate the embrittling effect of the interstitials during deformation. Given such a mechanism, a similar ductility enhancement would be expected for other alloying elements having larger atomic radii than Ni that nevertheless displace Ni to the 'Al' sublattice. The reported ductility enhancement for dilute amounts of other alloying elements, such as Ga and Mo, might also result from these elements displacing Ni to the 'Al' sublattice as a result of configurational entropy [3]. The proposed mechanism suggests that Pd might also have a ductilizing effect on Al-deficient $Ni_{50}Al_{40-x}Pd_x$. The thermodynamic calculations of Kao et al. [36] suggest that Pd should occupy the 'Ni' sublattice exclusively, displacing Ni to the 'Al' sublattice in Al-deficient alloys; ALCHEMI measurements confirm these predictions [41]. Since Pd occupies the 'Ni' sublattice exclusively in Pd-doped NiAl, ($Pd_{\cdot Ni'}$, $Ni_{\cdot Al'}$) defect pairs result from each Pd atom substituted for Al in NiAl, so that Pd should be an efficient agent for the production of these stress dipoles. Also, since the production of such stress dipoles does not rely on configuration entropy, these defect pairs can be produced at higher alloying concentrations than in $Ni_{50}Al_{40-x}Fe_x$.

5. Summary and conclusions

The site-distributions of Fe alloying additions to B2-ordered NiAl alloys have been measured by ALCHEMI (atom location by channeling-enhanced microanalysis). Twelve alloy compositions were examined, of stoichiometries $Ni_{50-x}Al_{50}Fe_x$ (Ni-deficient), $Ni_{50}Al_{50-x}Fe_x$ (Al-deficient), and $Ni_{50-x/2}Al_{50-x/2}Fe_x$ (intermediate), with four different alloying levels, $x=0.25$, 2, 5, and 10. The data indicate that Fe tends to act as a buffer between the two sublattices, preferentially occupying the site of the stoichiometrically deficient host element. However, the Fe alloying addition was found to partition between the two sublattices to some extent in all alloys, giving rise to nickel-site vacancies or nickel anti-sites defects. These point-defect concentrations increase as the alloying level (x) increases. The ALCHEMI results have been shown to compare well with published experimental studies using nonspectroscopic measurements, including extended X-ray absorption fine structure (EXAFS), magnetic susceptibility and nuclear magnetic resonance (NMR) measurements, vacancy and hardness measurements, and with the results of thermodynamic,

ab-initio and tight-binding calculations. A sharp increase in the 'Ni' site occupancy of Fe in the Al-deficient alloys at the 0.25 at% alloying level relative to the higher alloying concentrations suggests that the range of compositions reported by Darolia et al. [3] to exhibit enhanced ductility may coincide with an inversion in the site-substitution behavior, where more Ni than Fe occupies the 'Al' sublattice. A mechanism by which this inversion in site substitution may effect the observed ductility enhancement is proposed, based on elastic interaction between substitutional and interstitial point defects. Given this mechanism, the ductility enhancement reported by Darolia et al. might also be expected to result from the substitution of Pd for Al in NiAl.

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