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SOLUTE HARDENING AND SOFTENING EFFECTS IN B2 NICKEL ALUMINIDES

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Abstract

The effect of substitutional solute additions including Fe, Mn, and Pd on the hardness of B2-ordered NiAl alloys was investigated. The solid solution hardening behavior of intermetallics is more complex than that of typical metallic solid solutions because of complications arising from the site preference of the solute as well as the effects of the solute on the concentrations of other point defects, e.g. vacancies and anti-site defects. For this reason, care was taken to experimentally establish solute site preferences and point defect concentrations in the NiAl alloys before analyzing the hardness data. By taking these factors into account it was possible to rationalize the observed unusual hardening effects. Three distinct categories of solid solution hardening behavior were encountered. The first was hardening by the solute addition itself. This was observed in the case of Pd additions to Al-poor NiAl. However, when Fe or Mn is added to Al-poor NiAl a second category is observed; these elements are seen to *soften* the material. The third category of behavior is observed when Fe is added to NiAl with a constant Al concentration of 50 at. %. In this case it is vacancies, rather than solute atoms, which harden the material.

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1.0 Introduction

Efforts to improve the mechanical properties of intermetallic alloys often involve the use of interstitial or substitutional alloy additions. For example, in the case of nickel aluminides with the B2 crystal structure such alloying has been shown to significantly affect mechanical and physical properties including yield strength, diffusivities, creep strength, etc. [1,2]. Of interest in the present study will be the solid solution hardening (SSH) effects of substitutional alloy additions. The ordered nature of intermetallic alloys provides interesting complications in considering SSH which are not a concern in simple metallic solid solutions. One complication is that the solute addition may preferentially occupy one or more distinct sublattices affecting the hardness in different ways. For example, in the case of Fe additions to B2-ordered NiAl, the Fe atoms may occupy either the Ni or the Al sublattice depending on composition [3,4]. Another complication is that in many intermetallic compounds there are numerous point defects present, e.g. anti-site defects and vacancies [5]. These defects arise from constitutional as well as thermal sources and contribute their own hardening effects in the material. For example, off-stoichiometric hardening in NiAl has been attributed to Ni anti-sites and vacancies at Ni-rich and Al-rich compositions, respectively [6]. Also, thermal vacancies play a strong role in controlling the hardness of FeAl [7,8]. The addition of a solute element can significantly alter the concentrations of these point defects, strongly affecting the hardness in an indirect manner. With the presence of multiple types of hardening sources (solute elements as well as point defects), yet another question arises. Are the effects of multiple hardeners independent, or do they correlate in some fashion? It is clear that understanding SSH in intermetallic compounds is a challenging one.

In the present manuscript some of the above considerations will be addressed. Using the B2 NiAl phase as a matrix, the effect of substitutional additions including Fe, Mn, and Pd will be examined. The work on Fe-containing alloys has been conducted previously [9], but will be used in this manuscript for comparative purposes. Attention will be given first to establishing the site occupations and defect concentrations that arise as a result of the alloying. This information will then be applied to interpreting the observed SSH effects.

2.0 Experimental

Seven alloys of composition $\text{Ni}_{60-x}\text{Al}_{40}\text{M}_x$ (where $\text{M} = \text{Mn}$ or Pd and $x = 0, 2.4, 6,$ and 12) were prepared from high-purity starting elements by arc melting on a water chilled copper hearth. Only the binary alloy and the Mn-containing alloys were subsequently drop cast into water chilled copper molds. The ingots were then given a homogenization heat treatment of 10

hours at 1250°C in vacuum ($\sim 10^{-4}$ Pa). A secondary heat treatment of 5 hours at 1000°C was given in a dynamic argon atmosphere followed by water quenching. Fine powder (-325 mesh) was prepared from the quenched ingots for x-ray lattice parameter measurements. Coarse powder (-40 +80 mesh) was prepared for density measurements. The ingots were also sectioned to produce hardness specimens and TEM specimens for the ALCHEMI (atom location by channeling enhanced microanalysis) analysis.

X-ray diffraction was performed using Cu K α radiation. Scans were taken over a 2θ range of 50 to 138°. Silicon was used as an internal standard. The lattice parameter was calculated using 6 to 9 peaks. Density measurements were performed using a helium pycnometer, yielding an uncertainty better than 0.1%. The measurements were made using a coarse powder to eliminate the problems with porosity in cast NiAl noted by Helfrich and Dodd [10]. The hardness was measured using a Vickers indenter. Hardness values were converted to load over *projected* area and are reported in GPa. The ALCHEMI analysis was performed as part of a larger study [11], so the experimental details will not be given at this time. The technique used was similar to that developed by Anderson [12].

The experimental procedures used in the investigation of the Fe-containing NiAl alloys can be found in our previous work [9]. The hardness values of these Fe-containing alloys were measured again as part of the present study. This was done so that all reported hardness values would be taken from the same experimental apparatus. The differences in the two data sets were small, with the data of the present study being consistently around 5 to 7% higher than the prior data.

3.0 Results and Discussion

Since it is imperative that the site occupancies of alloying elements and their effect on the concentrations of other point defects first be known before a discussion on SSH effects can be attempted, this section will be divided into two parts. The first will be related to site occupancies and point defects, while the second will be on the resultant hardening effects.

3.1 Site Occupancies and Defect Concentrations

Point defects in NiAl consist mainly of Ni atoms on the Al sublattice (Ni anti-site defects) and vacancies on the Ni sublattice; this is the so-called triple defect structure [5,13]. Deviations from stoichiometry are accommodated by Ni anti-sites at Ni-rich compositions and vacancies at Al-rich compositions [14]. NiAl is a very strongly ordered compound and as a result there are relatively few thermal defects present compared to many other intermetallics

[5,15]. The solute-containing NiAl alloys considered in this manuscript lie in two different stoichiometric regimes. The first is the "Al-poor" alloys which have a constant 40 at. % Al. These alloys are characterized by the large amount of constitutionally necessary anti-site defects. The other regime is the "stoichiometric" alloys, having a composition of a constant 50 at. % Al. No constitutional defects are required in these alloys.

3.1.1 Al-poor alloys (40 at. % Al). These alloys are of the composition $\text{Ni}_{60-x}\text{Al}_{40}\text{M}_x$ where the ternary addition, $\text{M} = \text{Fe}, \text{Mn}, \text{or Pd}$. Of first interest is the site preference of the ternary element. Using a thermodynamic model, Kao et al. predicted that in these cases Fe and Mn would preferentially occupy the Al sublattice while Pd would occupy the Ni sublattice [16]. In agreement with these predictions, Fe additions to Al-poor NiAl alloys have been experimentally shown to exhibit a preference for the Al sublattice using the ALCHEMI technique [3,4,17,18]. However, a small amount of Fe was found to occupy the Ni sublattice as well. More recent ALCHEMI investigations by Anderson and Pike [11] have further supported the predictions of Kao et al. by finding that Mn preferentially occupies the Al sublattice, while Pd occupies the Ni sublattice exclusively (to within the precision of the measurement).

The next concern is how the ternary addition affects the concentrations of other point defects in the material. In order to accommodate the deviation from stoichiometry in binary $\text{Ni}_{60}\text{Al}_{40}$ it is necessary that 10 at. % Ni be present on the Al sublattice as constitutional defects. This can be represented by the following sublattice distribution notation: $[\text{Ni}_{50}]^{\text{Ni}}[\text{Al}_{40}\text{Ni}_{10}]^{\text{Al}}$, where the first bracket represents the Ni sublattice and the second bracket represents the Al sublattice. When the ternary addition M is added, the amount of Ni anti-sites may decrease or stay the same depending on the site preference of the addition. If M absolutely preferred the Al sublattice, the Ni anti-sites would be replaced by the M atoms and the sublattice distribution would look like this: $[\text{Ni}_{50}]^{\text{Ni}}[\text{Al}_{40}\text{Ni}_{10-x}\text{M}_x]^{\text{Al}}$. However, in the case of Fe and Mn additions where most, but not all, of the ternary addition goes to the Al sublattice, the sublattice distribution is more complicated: $[\text{Ni}_{50-y}\text{M}_y]^{\text{Ni}}[\text{Al}_{40}\text{Ni}_{10+y-x}\text{M}_{x-y}]^{\text{Al}}$, where $x > 2y$. Even with this complication, it is clear that as the ternary element M is added the Ni anti-site concentration decreases. In the case of an addition like Pd which exclusively occupies the Ni sublattice, the Ni anti-site concentration is unaffected and the sublattice distribution can be represented as: $[\text{Ni}_{50-x}\text{Pd}_x]^{\text{Ni}}[\text{Al}_{40}\text{Ni}_{10}]^{\text{Al}}$. It should be mentioned that the above discussion is based on the assumption that the vacancy concentrations in these alloys are small in comparison to the other types of point defects. This assumption will be shown to be valid in the following paragraphs.

The lattice parameter of the Al-poor alloys is shown in Fig. 1 as a function of the amount of solute addition. All three elements increase the lattice parameter. Pd has the

Fig. 1 The lattice parameter of $\text{Ni}_{60-x}\text{Al}_{40}\text{M}_x$ alloys quenched from 1000°C , where the solute $\text{M} = \text{Pd}, \text{Mn}, \text{or Fe}$.

strongest effect, followed by Mn, and then by Fe. It is now desirable to estimate the lattice dilation ($=1/a[da/dc]$, where a is the lattice parameter and c is the defect concentration) caused by the various point defects present in these alloys. This can be accomplished using the data in Fig. 1. However, before this is done it is necessary to remember that in all these cases multiple types of defects are present. For this reason, it is helpful to assume that the dilations of multiple types of defects will add linearly (as would follow from Vegard's law). By making this assumption the lattice dilation of Fe atoms on the Al sublattice (denoted Fe^{Al}) has been estimated to be -0.018 [9]. The negative sign denotes that it is a contraction, an indication that the Fe anti-sites are smaller than the host atoms on the Al sublattice. Using the same type of calculation, the lattice dilation of Mn atoms on the Al sublattice (Mn^{Al}) is estimated to be 0.038 . (To make this calculation the lattice dilation of Ni anti-sites (Ni^{Al}) was taken as -0.076 as determined from binary NiAl [15].) Interestingly, this positive dilation suggests that the Mn anti-sites are larger than the host Al atoms. For the case of Pd atoms on the Ni sublattice (Pd^{Ni}) the lattice dilation is estimated to be 0.125 . This is a strongly positive dilation compared to the others. This strong positive dilation is to be expected considering that Pd atoms are considerably larger than the host Ni atoms which they replace. These estimated lattice dilations are summarized in Table 1.

The densities of the Fe, Mn, and Pd-containing alloys are shown in Fig. 2. Pd increases the density of the alloys, while Fe and Mn lower the density. These trends are expected since in

Table I The lattice dilations and hardening rates of point defects in solute-containing NiAl alloys

Defect	Site	Defect Notation	Lattice Dilation	Estimated Hardening Rate (GPa)	Experimental Hardening Rate (GPa)
Vacancy	Ni	$\square^{Ni}$	-0.081 [15]	—	G/4.1 [15]
Pd atom	Ni	Pd^{Ni}	0.125	G/6 to G/8	G/10
Fe atom	Ni	Fe^{Ni}	0.007 [9]	G/40 to 0	< G/60 [9]
Ni anti-site	Al	Ni^{Al}	-0.076 [15]	—	G/12 [15]
Fe “anti-site”	Al	Fe^{Al}	-0.018 [9]	G/25 to G/600	< G/50
Mn “anti-site”	Al	Mn^{Al}	0.038	G/16 to G/36	G/20

Fig. 2 The density of $Ni_{60-x}Al_{40}M_x$ alloys quenched from $1000^\circ C$, where the solute $M = Pd, Mn, \text{ or } Fe$.

the Pd case the heavier Pd atoms are replacing the lighter Ni atoms, while both Fe and Mn are lighter than Ni and thus lower the density.

Using the lattice parameter and density data it is possible to determine the vacancy concentration of a given alloy. Chang and Neumann described this technique in detail in their review paper of point defects in B2 compounds [5]. The vacancy concentration (where the vacancy concentration is defined as the number of vacancies per total number of atoms in the crystal) was calculated for the alloys using the data in Figs. 1 and 2. The results are shown in Fig. 3. The vacancy concentrations are quite low for most of the alloys, 0.003 (0.3%) or less, except for the highest doped Mn alloy which had a concentration of 0.005 (0.5%). Nevertheless, the vacancy concentrations are relatively low, particularly when compared to the 50 at. % Al alloys (also shown in Fig 3) which will be discussed in the following section.

Fig. 3 The vacancy concentration of $\text{Ni}_{60-x}\text{Al}_{40}\text{M}_x$ alloys, where the solute $\text{M} = \text{Pd}, \text{Mn}, \text{or Fe}$, as well as $\text{Ni}_{50-x}\text{Al}_{50}\text{M}_x$ alloys where $\text{M} = \text{Fe}$. All alloys were quenched from 1000°C .

3.1.2 Stoichiometric Alloys (50 at. % Al). The composition of these alloys is $\text{Ni}_{50-x}\text{Al}_{50}\text{M}_x$ where only the case $\text{M} = \text{Fe}$ will be considered at this time. We have defined these alloys as “stoichiometric” since no constitutional defects, i.e. vacancies or anti-site defects, are necessary. In this case the model of Kao et al. predicts that Fe will occupy the Ni sublattice preferentially [16]. This has been verified experimentally by Duncan and co-workers using the ALCHEMI technique [3,4,18]. If all of element M resided on the Ni sublattice, the sublattice

distribution would be: $[\text{Ni}_{50-x}\text{Fe}_x]^{Ni}[\text{Al}_{50}]^{Al}$. However, a residual amount of Fe was found to remain on the Al sublattice [3,4,18]. This residual Fe must be accommodated for in some fashion in order to maintain a site balance. One possibility is the generation of vacancies on the Ni sublattice (denoted $\square^{Ni}$). The suggested sublattice distribution could then be written as: $[\text{Ni}_{50-x}\text{Fe}_{x-y}\square_{2y}]^{Ni}[\text{Al}_{50}\text{Fe}_y]^{Al}$ where $x > 2y$. Indeed, the predicted increase in vacancy concentration with increasing Fe has been verified experimentally by Pike et al. [9]. The results of that study are shown in Fig. 3 where the vacancy concentration increases from 0.003 (0.3%) to 0.013 (1.3%) as the Fe concentration increases from 0 to 12 at. %. This is a substantial increase in the number of vacancies and will prove to be important when considering the SSH effects of these alloys.

3.2 Solid Solution Hardening in NiAl

As discussed in Section 3.1, the addition of a ternary alloying element to NiAl can result in a number of different responses with regard to the site occupancy of the element and its effect on other point defect populations. These different responses in turn strongly affect the SSH behavior of the alloying element. To illustrate this, consider Fig. 4 where the hardness of the NiAl alloys is plotted as a function of the solute concentration. For the case of Pd added to Al-poor alloys and of Fe added to stoichiometric alloys, the hardness increased. However, in the case of Fe and Mn added to Al-poor alloys the hardness decreased. That is, Fe and Mn cause *softening* in Al-poor NiAl. When the observed hardening/softening effects are rationalized by taking into consideration the site occupancies and point defect concentrations, the SSH behaviors can be grouped into three categories: 1) hardening by the solute element itself, 2) softening, and 3) vacancy hardening. These three SSH behaviors will be discussed separately in the following sections.

3.2.1 Hardening by the Solute Element Itself. Alloying elements classified in this category are similar to those in typical solid solutions in that the solute addition itself is responsible for the hardening. The specific case in this study is that of Pd added to Al-poor NiAl. These alloys had the composition $\text{Ni}_{60-x}\text{Al}_{40}\text{Pd}_x$. As discussed in Section 3.1.1, the sublattice distribution for these alloys is $[\text{Ni}_{50-x}\text{Pd}_x]^{Ni}[\text{Al}_{40}\text{Ni}_{10}]^{Al}$. It is seen from this distribution that there are two types of majority defects present: Ni^{Al} and Pd^{Ni} . However, the Ni^{Al} concentration is independent of the amount of Pd added to the alloy. The only defects that change concentration when Pd is added are the Pd^{Ni} defects. Thus, the hardening observed in Fig. 4 is solely due to the increasing Pd^{Ni} defect concentration.

Fig. 4 The hardness of $\text{Ni}_{60-x}\text{Al}_{40}\text{M}_x$ alloys, where the solute $\text{M} = \text{Pd}$, Mn , or Fe , as well as $\text{Ni}_{50-x}\text{Al}_{50}\text{M}_x$ alloys where $\text{M} = \text{Fe}$. All alloys were quenched from 1000°C .

The hardening from point defects in many binary B2 intermetallics has been found to correlate with the square root of the hardening defect concentration [15]. The square root relationship is one predicted by one of the classical solid solution hardening models for metallic solutions [19]. Further, in the case of anti-site type defects in B2 compounds, the normalized hardening rate, γ/G (where the hardening rate, γ , is defined as $dH/d\sqrt{c}$, H is the hardness, G is the shear modulus, and c is the defect concentration), has been shown to linearly correlate with the lattice dilation of the hardening defect [15]. This suggested the elastic size effect plays a dominant role in the hardening. It is likely that the hardening due to solute additions to B2 compounds also follows these trends. However, it is necessary to have a method to add the hardening effects when multiple hardening sources are present (recall that there are both Ni^{Al} and Pd^{Ni} defects in this case). One method is the "mean square law" proposed by Koppelaar and Kuhlmann-Wilsdorf [20]. The mean square law can be adapted to apply to hardening in B2 intermetallics as has been done by Pike et al. [9]. The resulting equation is:

$$\Delta H = \sqrt{(\gamma_1 c_1^{1/2})^2 + (\gamma_2 c_2^{1/2})^2 + \dots + (\gamma_n c_n^{1/2})^2} \quad [1]$$

where ΔH is the increase in hardness, γ_x and c_x are the hardening rate and defect concentration, respectively, of the defect of type x , and n is the total number of different types of defects. It is

now possible to quantitatively rationalize the hardening data in Fig. 4. The hardening rate of Ni^{Al} defects has been found to be approximately $G/12$ [15] where the shear modulus, $G = 70$ GPa [21]. Since the lattice dilation of Pd^{Ni} defects was estimated earlier in this manuscript, it is possible to predict a hardening rate for these defects based on the linear relationship between the hardening rate and the lattice dilation [15]. Using that relationship, a hardening rate between $G/6$ and $G/8$ is predicted. By using Eq. [1] and the hardening rates of Ni^{Al} and Pd^{Ni} defects, the hardness can be estimated as a function of Pd concentration. When this calculation was performed, it was found that Eq. [1] does indeed predict the hardening behavior satisfactorily. However, a hardening rate for Pd^{Ni} defects of $G/10$ best described the data. This value is smaller than the predicted value, but is not excessively discrepant.

3.2.2 Softening. In Fig. 4 it was seen that Fe and Mn additions to Al-poor NiAl induced the unusual effect of softening rather than hardening. To understand why this softening occurs it is necessary to consider the effect of the solute additions on the concentrations of all of the point defects present in these alloys. Recall that the composition of these alloys was: $\text{Ni}_{60-x}\text{Al}_{40}\text{M}_x$ where $M = \text{Fe}$ or Mn , and the sublattice distribution was: $[\text{Ni}_{50-y}\text{M}_y]^{\text{Ni}}[\text{Al}_{40}\text{Ni}_{10+y-x}\text{M}_{x-y}]^{\text{Al}}$. It can be seen that there are three types of point defects present in these alloys: M^{Ni} , M^{Al} , and Ni^{Al} . Since the amount of M^{Ni} defects has been found to be small [17,18] and the hardening rate is expected to be small [9], it is reasonable to ignore these defects in discussing the SSH effects. This being the case, there are two defects to consider: Ni anti-sites, Ni^{Al} , and what we will define as “solute anti-sites”, M^{Al} . In these 40 at. % Al alloys it is necessary that the sum of the Ni and solute anti-site concentrations be 10 %. As a result, the concentration of Ni anti-sites decreases as that of solute anti-sites increases (that is, as solute is added to the material).

We know that the Ni anti-site is an effective hardener. It is now useful to estimate the hardening rates of the “solute anti-sites”. In Section 3.1.1 the lattice dilation of Fe and Mn additions were found to be -0.018 and 0.038 , respectively. By using the linear relationship between hardening rates and lattice dilations [15], the hardening rate of Fe anti-sites in NiAl was estimated to be between $G/600$ and $G/25$ [9]. In a similar manner, we can now estimate the hardening rate of Mn anti-sites in NiAl to be between $G/16$ and $G/36$. It is clear that both Fe and Mn anti-sites are expected to be considerably less potent hardeners than are the Ni anti-site defects. However, between the Fe and Mn anti-sites, the Mn anti-site should be the more potent hardener. By regarding the relative hardening rates it is now possible to rationalize why softening has been observed in these alloys. Consider, as solute is added to Al-poor NiAl the solute anti-site atoms begin to replace the Ni anti-sites. Less potent hardeners replace more potent hardeners, the net result being the observed softening effect seen in Fig. 4. This idea

was first proposed to describe the effects of Fe additions [9], but now appears to be equally effective for describing the effects of Mn additions.

It is interesting to see whether Eq. [1] adequately describes the softening behavior. We will use the known hardening rate of Ni anti-sites, and the anti-site concentrations as determined from ALCHEMI data [17,18]. With this information, we can use Eq. [1] to optimize the hardening rates of the Fe and Mn anti-site defects. The result is shown in Fig. 5 where the hardness as calculated from Eq. [1] is plotted against the square root of the Ni anti-site concentration along with the experimental data. It is seen that the equation describes the hardness data fairly well for both Fe and Mn additions. The optimized hardening rates of $G/20$ and $<G/50$ for Mn and Fe anti-sites, respectively, are well within the ranges estimated from the lattice dilations (see Table 1) and agree with the prediction that the Mn anti-site would be a more potent hardener than the Fe anti-site. Further, note that the hardness of the Fe-containing alloys is seen to fall along a line when plotted against the square root of the Ni anti-site concentration. The slope of this line is very close to the known hardening rate of Ni anti-site defects ($G/12$). This is evidence that the Ni anti-sites are effectively the sole source of hardening in this case and that the negligible Fe anti-site contribution can be ignored in Eq. [1]. This is not true for the Mn-containing alloys, however. If the Mn anti-site contribution were dropped from Eq. [1] the predicted hardness would essentially be the same as the Fe-containing alloys. Thus, the higher observed hardness values of the Mn-containing alloys clearly indicate a hardening contribution from the Mn anti-site defects.

Fig. 5 A comparison of hardness values estimated from Eq. [1] to the experimental data for the Al-poor alloys with Mn or Fe additions.

3.2.3 Vacancy Hardening. The third category of SSH behavior observed in NiAl alloys occurs in "stoichiometric" alloys with Fe additions, of composition $\text{Ni}_{50-x}\text{Al}_{50}\text{Fe}_x$. Recall that the sublattice distribution in these alloys was: $[\text{Ni}_{50-x}\text{Fe}_x\text{□}_{2y}]^{\text{Ni}}[\text{Al}_{50}\text{Fe}_y]^{\text{Al}}$. There are three potentially hardening defects, Fe^{Ni} , Fe^{Al} , and □^{Ni} . However, it has been suggested that the significant hardening observed in Fig. 4 cannot be rationalized by either Fe^{Ni} or Fe^{Al} defects since these are expected to be relatively weak hardeners [9]. Instead, it was proposed that the hardening is occurring as a result of the increasing vacancy concentration. Vacancies are known to cause significant hardening in B2 intermetallics, having hardening rates on the order of $G/4$ [15]. As a result of the vacancies being such potent hardeners, when Eq. [1] is used to describe the hardness data it becomes apparent that the only important term is that of vacancies. Thus, Eq. [1] reduces to a simple square root dependence of the hardness on the vacancy concentration. This is seen when considering Fig. 6 where the hardness of these Fe-doped stoichiometric alloys is plotted as a function of the square root of the vacancy concentration. A linear relationship is observed. Thus, in this class of alloys hardening occurs with addition of Fe, but the hardening is a result of the increase in vacancy concentration caused by the addition of Fe rather than the Fe itself.

Fig. 6 The hardness of $\text{Ni}_{50-x}\text{Al}_{50}\text{Fe}_x$ alloys (quenched from 1000°C) vs. the square root of the vacancy concentration [9].

4.0 Conclusions

1. Solid solution hardening by Fe, Mn, and Pd additions to B2-ordered NiAl was considered. Careful attention was given to establishing solute site occupancies as well as to measuring point defect concentrations affected by the solute additions.
2. The different site occupancies as well as the different effects on point defect populations of the various solute additions led to unusual hardening effects. These can be grouped into three distinct categories: hardening by the solute element itself, softening, and vacancy hardening.
3. In the case of Al-poor NiAl alloys with Pd additions, the Pd was found to exclusively occupy the Ni sublattice. These Pd^{Ni} defects were effective hardeners due to a substantial lattice dilation. This is a case of hardening by the solute element itself.
4. Softening was observed in Al-poor alloys with either Fe or Mn additions. The Fe and Mn atoms preferentially occupy the Al sublattice, replacing the Ni anti-site defects located there. Since the Fe and Mn anti-sites are considerably less potent hardeners than the Ni anti-sites, a net effect of softening was observed.
5. In the case of Fe added to NiAl with a constant Al concentration of 50 at. %, the observed hardening with increasing solute concentration results from the corresponding increase in vacancy concentration rather than from the increase in the concentration of the Fe additions themselves.

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